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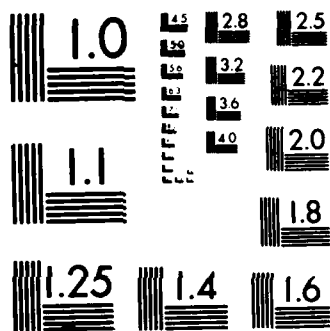   CONCRETE(U) NEW MEXICO ENGINEERING RESEARCH INST
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ESL-TR-85-68

Determine Parameters Causing Water Damage to Asphalt Concrete

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This report summarizes research involving the determination of parameters causing water damage to asphalt concrete. The study was a cooperative effort between the Federal Highway Administration (FHWA) and NMERI. Bituminous mixtures with a history of water susceptibility were fabricated by FHWA. Compacted mixtures were evaluated for moisture damage at FHWA, then shipped to NMERI for chemical analysis of the binders. Extracted binders were analyzed by a modified Clay-Gel procedure and infrared spectroscopy to determine whether differences between moisture conditioned and control asphalts could be measured. An Index of Relative Severity (water damage) has been defined from analysis of the data. Changes in certain asphalt chemical constituents may relate to retained strength for mixtures without anti-stripping additives. Potential moisture damage is predicted equally with at least two mechanical tests used for mixtures containing antistripping compounds.

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PREFACE

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

OBJECTIVE

The objective of this research effort was to study the effect of water on asphalt-aggregate compacted mixtures by changes in the fractions obtained from Clay-Gel analyses and functional group analyses of the extracted binder and Clay-Gel fractions before and after water treatment using infrared analysis.

BACKGROUND

Water damage is a serious problem encountered in the performance of flexible pavements. Stripping can result from the rupture of the adhesive bond at the asphalt-aggregate interface and water damage is one of the mechanisms that can result in stripping. Stripping is the most visible physical effect of water damage and is not a well-understood phenomenon. Water that penetrates asphalt concrete can displace polar molecules adsorbed at the asphalt-aggregate interface and break the adhesive bond (Reference 1). If the aggregate has a greater affinity for the water than the polar asphalt molecules, the bond between binder and aggregate will be replaced by a water-aggregate bond.

Investigation of the effects of water on the interaction between binder and aggregate is necessary to gain a more fundamental understanding of the chemical processes that result in stripping. Asphalt can be separated by the Clay-Gel method of compositional analysis (ASTM D-2007-75, with modifications--see Appendix A) into four fractions: asphaltenes, polars, aromatics, and saturates, which are listed here in order of decreasing polarity. Certain functional groups present in the polar fractions are selectively adsorbed onto the aggregate and may be displaced by the action of water (Reference 1). The mechanism for this action is not well understood and is difficult to study because of the complexity of asphalt-aggregate systems. However, infrared spectroscopy (IR) has proven useful for studying the effect of water via functional group analysis of asphalt extracted from asphalt-aggregate compacted mixtures. This technique was used in this study to identify changes in functional group concentrations occurring after exposure of asphalt concrete briquets to water treatment. A more detailed explanation of IR principles and how it is used to relate the findings to the water damage problem is discussed later in this report.

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SCOPE

To find methods or treatments that will reduce the possibility of water
damage, or to develop products that will not be susceptible to damage from
water, one must first understand the fundamental chemical processes involved
in water, binder, and aggregate interactions. This research effort was aimed
at establishing a basic understanding of the chemical changes resulting from
exposure to water. Clay-Gel analysis was used to investigate changes occuring
in each generic fraction of the asphalt binder. Infrared spectroscopy was
used to determine which functional groups were affected by water in select
Clay-Gel fractions and whole extracted and virgin binders.

METHOD

This research was divided into two phases. Phase I included the litera-
ture review, development of the test matrix, water damage treatment, and Clay-
Gel analyses. Phase II consisted of further Clay-Gel analyses and functional
group analyses by infrared spectroscopy.

An investigation of the literature and current research related to water
damage studies and asphalt-aggregate interactions was completed. This data
base provided a starting point for this research. The original proposed NMERI
test matrix included the variables of crude source, asphalt cement grade, and
stripping and nonstripping aggregates. However, before the NMERI test matrix
was implemented, it was learned that the Federal Highway Administration (FHWA)
was performing a similar study on water damage of bituminous mixtures by
investigating physical parameter changes. A cooperative effort between FHWA
and NMERI resulted from discussions between the two groups. At this point,
NMERI implemented the test matrix formulated by the FHWA. This test matrix is
discussed in Section III. FHWA prepared Marshall and Immersion-Compression
specimens and tested them for physical properties. These specimens were sent
to NMERI for extraction and chemical analyses. The physical and chemical
changes were documented and are analyzed in this report.

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WATER DAMAGE STUDIES

Pavement distress caused by the action of water is relatively easy to identify. However, reasons for the effect water has on some asphalt concretes is not readily explained. In fact, attention of researchers to the causes of water damage has been equally divided between the asphalt, the aggregates, the interaction between these materials, and construction procedures. This little-understood mechanism is probably affected by many parameters, and therefore, like so many other pavement distress modes, is difficult to model and predict in the laboratory. The complexity of this phenomenon can be demonstrated by the diversity of approaches undertaken by various investigators. These have included development of test methods to evaluate mechanical consequences of disbonding, fundamental studies involving wetting behavior of asphalts, and studies of the effects of water on chemical interactions of asphalt with aggregate. Water damage to bituminous mixtures manifests itself in both the microscopic and macroscopic scale. Moisture-induced damage is considered (Reference 1) to be related to the initial rupture of the adhesive bond and may reform if the water has a means of escape. The terminal breaking of the adhesive bond between the aggregate surface and the asphalt binder is known as stripping (Reference 2).

Moisture mechanisms which cause damage to asphalt concrete mixtures have been the subject of many studies. Lottman (Reference 3) and other researchers list the following as the causes of water damage to bituminous pavement mixtures:

1. Pore pressure in the mixture due to wheel-loading repetitions, thermal expansion-contraction differences due to ice formation, temperature cycling above freezing, freeze-thaw and thermal shock, or a combination of these factors.

2. Asphalt removal by water in the mixture at moderate to high temperatures.

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3. Water-vapor interaction with the asphalt-filler mastic and larger aggregate interfaces.

4. Water interaction with clay minerals in the aggregate fines.

5. Hydrogenesis.

6. Physio-chemical properties of the asphalt-aggregate materials.

7. Design/construction quality.

Taylor and Khosla (Reference 2) suggest several mechanisms by which stripping may occur and include the following: detachment, replacement, spontaneous emulsification, pore pressure, and hydraulic scouring. They also list factors which can influence stripping: type and use of mix, asphalt characteristics, aggregate characteristics, environment, traffic, and construction practice. A brief description of each of the suggested influential factors is outlined below.

Type and Use of Mix

The occurrence of stripping has been more pronounced in open-graded mixes, base courses, and surface treatments, all of which are relatively permeable to water, when compared to dense-graded mixes. Mixes with high air voids, insufficient bitumen, aggregates that are susceptible to stripping, and/or are inadequately compacted may also be prone to stripping problems.

Asphalt Characteristics

Viscosity of asphalts has been the most prominent characteristic studied in stripping of pavement mixtures. Resistance to stripping has generally been observed to increase with asphalt viscosity (References 4 and 5). Pull tests (Reference 4) revealed that asphalts with low viscosity stretch further than those with high viscosity. Also, the lower the viscosity, the greater the wetting power of the asphalt for aggregate surfaces (Reference 6). The relationship of the chemical composition of asphalts to stripping is not well-defined in the literature. However, Dohaney (Reference 7) and Chehovits et al. (Reference 8) have observed that asphalt composition, as determined by the Rostler method, can affect water-resistance of asphalt concrete. These

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authors observed from laboratory studies that mixtures designed with binders consistiny of low nitrogen bases, high acidaffin content, and low asphaltenes sustained better antistripping characteristics. Other researchers (Reference 6) believe that large quantities of paraffins and/or saturates* can be detrimental to water-damage resistance. However, there is no indication in the literature regarding a maximum level of saturated hydrocarbons in an asphalt system which can be tolerated before suffering water damage. Finally, the refinery process by which the asphalts are produced can alter the chemical composition.

Aggregate Characteristics

The mineralogical and chemical composition of the aggregate are important factors in the susceptibility of an asphalt mixture to stripping in the presence of water. The chemical properties of the aggregate affect its surface energy, chemical reactivity, and the nature and presence of adsorbed coatings (Reference 9). The variation of the surface chemistry between different aggregates affects the relative selectivity of the aygregate bonding sites for water or asphalt polar molecules.

Asphalt-Aggregate Interactions

Petersen and coworkers (References 1, 10, and 11) characterized polar functional groups present in asphalt that are found to be adsorbed on aggregate surfaces and may be displaced by water. These polar functional groups include carboxylic acids, dicarboxylic anhydrides, sulfoxides, basic nitrogen types (pyridinic type compounds), 2-quinolone types, and ketones. These functional groups are arranged in order of decreasing relative affinity for aggregate surfaces and may reorder slightly depending on the specific aggregate used. The relative susceptibility of these compounds to be displaced from the aggregate by water is reported to be in the same general order (References 1, 10, 11, 12, and 13). Nitrogen-containing compounds are suspected of playing a major role in determining the degree of water damage to an asphalt-aggregate mixture (References 1 and 13). Pyridine treatment of moisture-sensitive aggregates improved the water resistance of corresponding asphalt-aggregate mixtures. Addition of pyridinic-type compounds derived from shale oil

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*From Discussions with L. W. Corbett, 1985 .

residues to asphalt showed similarly improved water resistance in asphalt-aggregate mixes (Reference 1). However, the interaction between asphalt and aggregate that determines a water-resistant bond is dependent on a number of highly variable parameters such as asphalt composition, aggregate chemistry and surface characteristics, and the conditions in which the bond is allowed to form.

Environment

The environment of an asphalt pavement is the dominant factor contributing to the occurrence or absence of stripping. Seasonal temperature variations have adverse effects on the resistance of pavement structures against water damage. Even the variation between day and night temperatures can have a measurable impact on the resistance of a pavement to stripping. Researchers (Reference 5) have shown that the degree of water damage to a pavement mixture is proportional to the level of water content in the pavement.

Traffic

Hydraulic scouring due to the action of vehicle tires on saturated pavement surfaces promotes stripping. Highway lanes which carry heavy traffic have a tendency to strip in areas of heavy precipitation or poor drainage (References 4 and 14). However, the overall effect of traffic on asphalt stripping is not clearly understood although the cyclic loading effect can be considered a contributing factor.

Construction Practice

Good compaction and weather conditions during construction are prerequisites to the prevention of water stripping. Pavements which are constructed in late fall, in cool and damp weather, or with high air voids are reported to be more susceptible to stripping (Reference 15). Maupin (Reference 16) and other researchers state that there is no single cure or rehabilitation solution to all water damage-related pavement problems. However, quality compaction, assuming good materials are available, plus good weather conditions and low air voids can assure increased resistance of pavement to water damage.

Many investigators have developed physical methods for the determination of the effects of water damage to asphalt concrete mixtures. These methods

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test for the bulk behavior of mixtures. Some of these methods include the Lottman Moisture Damage Test (References 3 and 17), NCHRP-Project 10-17 Method (Reference 18), Immersion-Compression Method (Reference 19), Water Suscepti-bility Test (Reference 20), and the Texas Pedestal Test (References 21, 22, and 23). Scrimsher (Reference 24) lists the Moisture Vapor Susceptibility Test, Swell Test, Sand Bath Test, and Capillary Absorption Test as other methods which can be used to evaluate moisture damage effects in bituminous mixtures. Goetz (Reference 25) lists the following classification scheme of test methods for water resistance of bituminous mixtures:

1. Tests which measure surface activity or interfacial tension.

2. Coating or mixing tests in the presence of water.

3. Static immersion tests.

4. Immersion tests employing agitation-wash tests.

5. Water displacement tests employing hot or boiling water with or without electrolytes.

6. Tests which measure change in volume on exposure to water (swell tests).

7. Tests which measure strength properties before and after water exposure.

8. Simulated traffic tests (track tests).

Some of the methods listed above have gained various degrees of acceptance in the user communities. To date, debate still persists with regard to which method best assesses the water damage potential of bituminous mixtures. The most widely used methods include the Lottman Test and the Immersion-Compression procedure. Both of these methods were applied to the materials evaluated in this study.

The application of either method listed above yields varying degrees of severity. The Lottman procedure is reported (Reference 26 and 27) to be the

most severe of all test methods, and the Immersion-Compression procedure, the least severe. The degree of severity is measured in various ways and may be expressed as a damage ratio, tensile strength ratio, resilient modulus ratio (References 17, 26, and 27), or the number of freeze-thaw temperature cycles until failure (References 20-23). Tunnicliff (Reference 28) defines the tensile strength ratio as follows:

$$\text{Tensile strength ratio (TSR)} = \frac{\text{Tensile strength (wet)}}{\text{Tensile strength (dry)}}$$

where tensile strength is determined by diametral splitting tension tests. Button et al. (Reference 26) defines resilient modulus ratio as:

$$\text{Resilient modulus ratio (RMR)} = \frac{M_R \text{ after moisture damage}}{\text{Original } M_R \text{ of the specimen}}$$

where resilient modulus is measured by the device developed by Schmidt et al. (Reference 5). Lottman (Reference 17) suggested that a tensile strength ratio below 0.70 indicates a moisture susceptible pavement mixture. Tunnicliff and Root (Reference 18 and 28) suggested modifications to the Lottman test procedures. These modifications include presaturation of specimens by a partial vacuum to about 55 percent, then moisture-conditioning of specimens at 140°F for 24 hours to a saturation level of about 80 percent. The diametral splitting test conditions were changed to a rate of 2 inches per minute at 77°F, whereas Lottman called for slower rates, lower test temperatures, and more severe vacuum and moisture-conditioning procedures. Published data and discussions with various researchers indicate that the modified procedure is adequate in determining water damage to bituminous mixtures (Reference 28). The Lottman procedure often conditions specimens to moisture levels exceeding 100 percent. This result is usually associated with a specimen volume change. Such specimens are considered to be structurally damaged (Reference 28). Button et al. (Reference 26) have provided information on long-term performance of bituminous mixtures using the Lottman procedure.

Gilmore et al. (Reference 27) used indirect tension and resilient modulus measurements in conjunction with the Lottman conditioning procedures to determine moisture effects on the durability of additive modified asphalt mixtures. The resilient modulus ratios were observed to be lower than the tensile strength ratios in the study. This result indicated that the resilient modulus test is more sensitive to moisture effects using the Lottman procedure (Reference 27).

Moisture damage to bituminous mixes is a serious problem. In fact, a number of state highway departments use antistripping agents routinely to reduce the sensitivity of the mixes to moisture damage. Many of these departments have not performed any research to verify the severity of the problem, or to assess the effect or need for antistrip additives. The development and use of test methods in research efforts illustrate that the problem of water stripping is of great concern. Mechanical property evaluations using these test methods have dominated the evaluation programs documented in the literature. Studies involving the mechanisms of water damage from a molecular viewpoint have been limited to functional group analyses using infrared spectroscopy. From these studies, polar asphalt molecules have been identified as the functional groups that adsorb most strongly on the aggregate. However, the relationship between the polar group concentrations and the bulk generic chemical composition of asphalts, and how this relationship affects water damage, has not been studied extensively. This research effort attempts to answer some of the questions from a chemical perspective. This evaluation consisted of materials supplied to the New Mexico Engineering Research Institute by the Federal Highway Administration. The discussion of these materials, as well as the testing program, is presented in Section III.

SECTION III
MATERIALS AND TESTING

MATERIALS

Asphalt cements, mineral aggregates, antistripping compounds, and asphalt concrete were evaluated in this study. Compacted asphalt mixtures were provided to NMERI by FHWA as part of this cooperative research effort. Mixtures were designed by the Marshall procedure (ASTM D1559) and fabricated both by the Marshall and methods described by ASTM D1174(30). Mixtures prepared from materials historically water-damage susceptible came from the participating states of Georgia, Mississippi, and Utah.

Mix designs representing each individual state were used to fabricate test specimens at FHWA. Materials used in the fabrication of test specimens are shown in Table 1. A general description of each material provided by FHWA is shown in Table 2.

Compacted mixtures from FHWA included both control and water exposed test specimens. Eight specimens were evaluated for materials from each state. Four specimens were controls (no water exposure) for both test procedures, two were subjected to ASTM D1075 (immersion compression) exposure, and two were subjected to Lottman (References 3 and 17) conditioning.

Asphalt concrete samples discussed in this report are labelled in the following manner:

```
          AC-30 ─┐           ┌─ Crushed Limestone
                 \           /
          GAR - 30Y - L1
                /           \
Georgia, Rome ─┘             └── Additive Type
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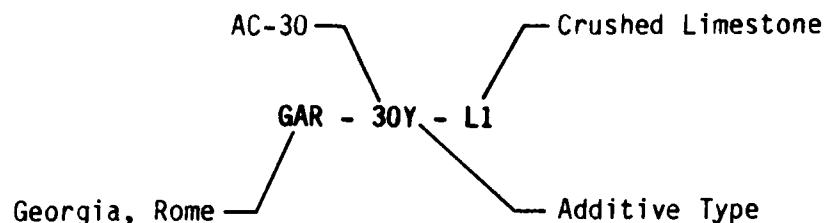
Asphalts, aggregates, and additives are designated by FHWA Laboratory Numbers as shown in Table 1.

TABLE 1. ASPHALT CEMENTS, ADDITIVES, AND AGGREGATES.

FHWA LAB NO.	DESIGNATION	LOCATION	AGGREGATES
B-5839	AC-20	GEORGIA	
B-5856	AC-30	GEORGIA	
		ROME	L1 – CRUSHED LIMESTONE
		KENNESAW	G1 – GRANITE GNEISS[a]
		GRAYSON	G1 – GRANITE GNEISS[a]
		NORCROSS	G2 – GRANITE GNEISS[a]
B-5851	AC-20	MISSISSIPPI	C – CHERT
B-5891	AC-10	UTAH	L2 – DOLOMITIC LIMESTONE
B-5877	ADDITIVE (W)	GEORGIA	
		KENNESAW	
		GRAYSON	
		NORCROSS	
B 5892	ADDITIVE (X)	MISSISSIPPI	
	ADDITIVE (Y)	GEORGIA	
		ROME	
	ADDITIVE (Z)	UTAH	

NOTES: Some of the binders were supplied preblended with additives.

Properties of the additives and binders are listed in Table 3.

a – Aggregates obtained from different quarries.

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TABLE 2. GENERAL DESCRIPTION OF TEST MATERIALS FROM FHWA

SAMPLE IDENTIFICATION	MIXTURE CHARACTERISTICS	TEST AND TREATMENT METHOD	AGGREGATE FIELD STRIPPING CLASSIFICATION
GEORGIA			
GAR-30-L1	100% CRUSHED LIMESTONE 6.25% AC-30	LTM-DRY	SLIGHT STRIPPER
		IC-WET	SLIGHT STRIPPER
GAR-30Y-L1	SAME MIX PLUS 0.75% ADDITIVE (Y) BY WEIGHT OF ASPHALT	LTM-DRY	NONSTRIPPER
		IC-WET	
GAK-30-G1	100% GRANITE GNEISS 6.4% AC-30	IC-WET	SEVERE STRIPPER
		LTM-DRY	
GAK-30W-G1	SAME MIX PLUS 1% ADDITIVE(W) BY WEIGHT OF AGGREGATE	LTM-DRY	
		IC-WET	
GAG-30-G1	100% GRANITE GNEISS 5.65% AC-30	LTM-DRY	SEVERE STRIPPER
		IC-WET	
GAG-30W-G1	SAME MIX PLUS 1% ADDITIVE(W) BY WEIGHT OF AGGREGATE	LTM-DRY	NONSTRIPPER
		IC-WET	
GAN-30-G2	100% GRANITE GNEISS 5.90% AC-30	LTM-WET	MODERATE STRIPPER
		IC-WET	
GAN-30W-G2	SAME MIX PLUS 1% ADDITIVE(W) BY WEIGHT OF AGGREGATE	LTM-DRY	NONSTRIPPER
		IC-WET	

TABLE 2.   GENERAL DESCRIPTION OF TEST MATERIALS FROM FHWA (CONCLUDED).

SAMPLE IDENTIFICATION	MIXTURE CHARACTERISTICS	TEST AND TREATMENT METHOD	AGGREGATE FIELD STRIPPING CLASSIFICATION
MISSISSIPPI			
MS1-20-C	70% CRUSHED CHERT 22% UNCRUSHED CHERT 8% SAND 4.5% AC-20	LTM-DRY	SLIGHT STRIPPER
		IC-WET	
MS2-20-C	SAME MIX DESIGN	LTM-DRY IC-WET	SLIGHT STRIPPER
MS2-20X-C	SAME MIX PLUS 0.3% ADDITIVE(X) BY WEIGHT ASPHALT	LTM-DRY	NONSTRIPPER
		IC-WET	
UTAH			
UT-10-L2	100% DOLOMITIC LIMESTONE 3.8% AC-10	LTM-DRY	SEVERE STRIPPER
		IC-WET	
UT-10Z-L2	SAME MIX PLUS 0.30% ADDITIVE (Z) BY WEIGHT OF ASPHALT	LTM-DRY	NONSTRIPPER
		IC-WET	

LTM = Lottman
IC = Immersion compression

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TESTING

The testing program involved characterization of asphalt cements with and without additives, and various combinations of compacted bituminous mixtures and recovered binders. The testing conducted in this cooperative effort involved physical and chemical evaluation to study relationships between chemical and physical effects of water damage. The test matrix for the cooperative effort will be presented under the FHWA testing subsection. The discussion in the following subsections presents the testing program conducted at FHWA and NMERI.

FHWA Testing

FHWA performed physical tests on compacted asphalt concrete mixtures before and after water exposure and on asphalt cements used to fabricate the mixtures. The resulting data and specimens were sent to NMERI. The physical parameters defined by FHWA included the following: (1) binder specific gravity at 77°F, (2) binder penetration at 77°F, (3) viscosity at 140°F and 275°F, (4) flash points using COC (Cleveland Open Cup), (5) bulk density of compacted mixes and designated as core gravity, (6) maximum theoretical specific gravity and designated as maximum gravity, (7) air voids, (8) dry strength (lb/in^2), (9) wet strength (lb/in^2), (10) percent retained strength, and (11) percent saturation. The test matrix showing materials tested in the cooperative program is shown in Figure 1.

NMERI Testing

NMERI conducted viscosity tests (ASTM D-2171) on the virgin and extracted binders from FHWA-fabricated test specimens. NMERI also conducted the chemical characterization of these binders using Clay-Gel analyses (ASTM D-2007-75), with modifications described in Appendix A. Functional group analysis using infrared spectroscopy was performed by Western Research Institute (WRI), University of Wyoming, Laramie.

Infrared spectroscopy is an absorbance spectroscopic technique that has been adopted by this research organization to analyze asphalts. It involves the absorption of radiation in the infrared region of the spectrum that results from the excitation of bond deformations in molecules. The amount of

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Figure 1. FHWA Cooperative Test Matrix.

energy required to cause bond deformations depends upon the masses of the atoms and on the strength of the bond between the atoms, therefore, certain functional groups such as carbonyls, alcohols, nitrogen containing groups, anhydrides, and/or sulfoxides will have characteristic bands in distinct areas of the spectrum. Small shifts in these bands occur depending upon the surrounding environment of the specific functional group. By selectively reacting the asphalt with specific reagents, the researchers can isolate the functional groups of interest in asphalt. The functional groups produced upon oxidative aging of asphalt include ketones, anhydrides, carboxylic acids and their salts, and sulfoxides. Quantitative IR analyses were performed on select materials before and after water treatment, and the concentration changes of these functional groups were calculated. The materials included in the IR analysis were Georgia virgin asphalt (AC-30), Mississippi virgin asphalt (AC-20), Georgia extracted binders, Mississippi extracted binders, and one polar fraction from each of the above materials.

In summary, the testing programs conducted at NMERI, FHWA, and WRI may provide information on the following variables:

1. Viscosity changes and its role in water damage.

2. Relative severity of water damage treatment methods.

3. Changes in percentages of the Clay-Gel fractions.

4. Functional group concentration changes.

5. Percent retained strength variations.

6. Effects of varying percent air voids.

7. Effects of additives.

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SECTION IV

RESULTS AND DISCUSSION

RESULTS

The results presented in this section include physical properties of asphalt concrete mixtures fabricated by FHWA and physical/chemical properties determined by NMERI.

Test Results

Physical properties of the virgin binders and compacted mixtures, both with and without additives, are listed in Tables 3, 5, 6, 7, and 8. Chemical data for the same materials are listed in Tables 3, 4, 5, 9, and 10. Throughout the remainder of this report, the Lottman and Immersion-Compression test procedures will be referred to as LTM and IC, respectively.

DISCUSSION

The discussion will present physical and chemical data separately, along with observed correlations. Some mixtures, particularly those without additives, experienced saturation levels in excess of 100 percent. This phenomenon has been observed by many investigators to be most pronounced with the Lottman-treated mixes. Some researchers (References 15 and 28) have interpreted the low tensile strengths obtained after saturation exceeds 100 percent as an indication of structurally damaged briquets. Personal discussions with other investigators indicated that saturation in excess of 100 percent may lead to softening of the binder causing loss of strength within the mix.

Physical Considerations

The physical properties of virgin binders, additives, and additive-modified binders are summarized in Tables 3 and 5. Figure 2 summarizes the relationship between additive-modified and virgin binders studied in this investigation. The relationship suggests that the additives used in this study did not noticeably affect the viscosity of the binder at 140°F. Figure 3 summarizes viscosity test results from Table 8 of extracted binders for

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TABLE 3. PHYSICAL PROPERTIES OF NEAT BINDERS AND ANTISTRIPPING AGENTS.

PHYSICAL PROPERTIES	NEAT BINDERS					ANTISTRIPPING AGENTS				
	B-5839	B-5851	B-5856	B-5891	INV	A[a]	B	C	D	INV
Specific gravity (77°F)	1.03	1.03	1.04	1.04	FHWA	2.34	1.03	0.95	0.98	MTI
Penetration (77°F)	84	84	72	96	FHWA	--	--	--	--	
Flash point, °F (COC)	505	545	500	575	FHWA	--	275[b]	275[b]	275[b]	MTI
Viscosity, cSt (275°F)	489	482	581	307	FHWA	--	--	--	--	
Viscosity, poises (140°F)	2363	2147	3566	1172	FHWA	--	--	--	--	
Viscosity, poises (140°F)	2361	2482	3594	ND	NMERI	--	--	--	--	
Viscosity, cSt (77°F)	ND	ND	ND	ND		--	750-2000	350-1050	400-1200	MTI

a -- Solid additive and specific gravity provided by FHWA.

b - Minimum value.

INV = Investigator

MTI = Manufacturers Technical Information

-- = Not available

ND = Not Determined

TABLE 4. INFRARED ANALYSIS OF NEAT BINDERS AND THE CLAY-GEL
POLAR FRACTION FOR ASPHALTS B-5851 AND B-5856.

FUNCTIONAL GROUP	B-5851		B-5856	
	NEAT	POLAR FRACTION	NEAT	POLAR FRACTION
Ketones +/- 0.02	0	0.014	0	0.10
Carboxylic acids +/- 0.005	0	trace	0.016	0.018
Carboxylate[a] salts	0	0	0	---
Sulfoxides +/- 0.02	0.05	0.20	0.03	0.16
Anhydrides[b]	0	0.014	0	0.009

Note: All concentrations are in moles/liter.

     a - determined by the difference;

        thus, the error is outside the limits of +/- 0.005

     b - peak distorted by ester impurities

TABLE 5. VISCOSITY AND CLAY-GEL COMPOSITION OF NEAT BINDERS
AND BINDERS PLUS ANTISTRIPPING AGENTS.

Sample ID	Viscosity[a]	% Asphaltenes[b]	% Saturates[c]	% Aromatics[d]	% Polars[e]	INV
B-5839	See	ND	ND	ND	ND	NMERI
B-5851		28.80	12.90	24.47	33.87	NMERI
B-5856	Table 3.	27.96	8.61	22.87	40.65	NMERI
B-5891		ND	ND	ND	ND	NMERI
B-5851 + X	2197 P	30.97	12.24	22.27	34.52	NMERI
B-5856 + Y	3849 P	31.45	7.95	18.94	41.67	NMERI
B-5891 + Z	1225 P	ND	ND	ND	ND	NMERI

a - Measured in Poises ($140°F$).

b - % Asphaltenes: +/- 0.76

c - % Saturates: +/- 0.63

d - % Aromatics: +/-1.12

e - % Polars: +/- 1.63

ID = Identification

INV = Investigator

ND = Not Determined

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TABLE 6. BASIC PROPERTIES OF COMPACTED MIXTURES.

SAMPLE	TEST METHOD	% ASPHALT	CORE SPECIFIC GRAVITY	MAXIMUM THEORETICAL SPECIFIC GRAVITY	% AIR VOIDS
GAK-30-G1	LTM	6.40	2.417	2.507	3.6
GAK-30-G1	IC	6.40	2.343	2.507	6.5
GAK-30W-G1	LTM	6.40	2.409	2.507	3.9
GAK-30W-G1	IC	6.40	2.352	2.507	6.2
GAG-30-G1	LTM	5.65	2.336	2.420	3.5
GAG-30-G1	IC	5.65	2.280	2.420	5.8
GAG-30W-G1	LTM	5.65	2.336	2.420	3.5
GAG-30W-G1	IC	5.65	2.290	2.420	5.4
GAN-30-G2	LTM	5.90	2.386	2.487	4.1
GAN-30-G2	IC	5.90	2.325	2.487	6.5
GAN-30W-G2	LTM	5.90	2.390	2.487	3.9
GAN-30W-G2	IC	5.90	2.335	2.487	6.1
GAR-30-L1	LTM	6.25	2.350	2.445	3.9
GAR-30-L1	IC	6.25	2.271	2.445	7.1
GAR-30Y-L1	LTM	6.25	2.350	2.445	3.9
GAR-30Y-L1	IC	6.25	2.295	2.445	6.1
MS1-20-C	LTM	4.50	2.304	2.381	3.3
MS1-20-C	IC	4.50	2.209	2.381	7.2
MS2-20-C	LTM	4.50	2.315	2.401	3.6
MS2-20-C	IC	4.50	2.232	2.401	7.0
MS2-20X-C	LTM	4.50	2.309	2.401	3.8
MS2-20X-C	IC	4.50	2.233	2.401	7.0
UT-10-L2	LTM	3.8	2.553	2.667	4.3
UT-10-L2	IC	3.8	2.503	2.667	6.1
UT-10Z-L2	LTM	3.8	2.561	2.667	4.0
UT-10Z-L2	IC	3.8	2.501	2.667	6.2

LTM = Lottman
IC = Immersion Compression

TABLE 7. STRENGTH PROPERTIES OF DRY AND WET COMPACTED MIXTURES.

SAMPLE	TEST METHOD	DRY STRENGTH (psi)	WET STRENGTH (psi)	% RETAINED STRENGTH	% WATER SATURATION
GAK-30-G1	LTM	129	38	29.5	175.0
GAK-30-G1	IC	348	211	60.6	71.5
GAK-30W-G1	LTM	126	98	77.8	105.7
GAK-30W-G1	IC	358	322	89.9	52.3
GAG-30-G1	LTM	143	6	4.2	461.1
GAG-30-G1	IC	393	76	19.3	207.4
GAG-30W-G1	LTM	146	135	92.5	82.6
GAG-30W-G1	IC	410	421	102.7	50.2
GAN-30-G2	LTM	135	48	35.6	129.0
GAN-30-G2	IC	371	271	73.1	71.2
GAN-30W-G2	LTM	141	117	83.0	89.2
GAN-30W-G2	LC	403	384	95.3	45.1
GAR-30-L1	LTM	117	88	75.2	79.5
GAR-30-L1	IC	325	275	84.6	42.9
GAR-30Y-L1	LTM	108	95	88.0	75.4
GAR-30Y-L1	IC	356	297	83.4	42.0
MS1-20-C	LTM	92	70	76.1	138.8
MS1-20-C	IC	203	170	83.7	64.3
MS2-20-C	LTM	92	78	84.8	115.5
MS2-20-C	IC	190	176	92.6	58.1
MS2-20X-C	LTM	86	72	83.7	114.9
MS2-20X-C	IC	175	174	99.4	54.7
UT-10-L2	LTM	139	107	77.0	83.1
UT-10-L2	IC	433	241	55.7	69.8
UT-10Z-L2	LTM	148	117	79.1	85.1
UT-10Z-L2	IC	425	371	87.3	56.7

LTM = Lottman
IC = Immersion Compression

TABLE 8. EXTRACTED BINDER VISCOSITIES.

SAMPLE	TEST AND TREATMENT METHOD	VISCOSITY AT 140°F, POISES	% EXTRACTED BINDER	% DESIGN BINDER
GAK-30-G1	LTM-D	8351	6.6	6.4
GAK-30-G1	LTM-W	8646	6.1	6.4
GAK-30-G1	IC-D	7936	6.2	6.4
GAK-30-G1	IC-W	8197	6.4	6.4
GAK-30W-G1	LTM-D	11577	6.2	6.4
GAK-30W-G1	LTM-W	16029	6.2	6.4
GAK-30W-G1	IC-D	10041	4.8	6.4
GAK-30W-G1	IC-W	16355	6.3	6.4
GAG-30-G1	LTM-D	9535	4.7	5.65
GAG-30-G1	LTM-W	11989	5.5	5.65
GAG-30-G1	IC-D	9695	5.4	5.65
GAG-30-G1	IC-W	6232	5.5	5.65
GAG-30W-G1	LTM-D	6847	4.7	5.65
GAG-30W-G1	LTM-W	13448	5.5	5.65
GAG-30W-G1	IC-D	NOT TESTED	5.4	5.65
GAG-30W-G1	IC-W	11756	5.4	5.65
GAN-30-G2	LTM-D	7689	5.8	5.9
GAN-30-G2	LTM-W	10255	5.5	5.9
GAN-30-G2	IC-D	10198	5.7	5.9
GAN-30-G2	IC-W	10297	5.6	5.9
GAN-30W-G2	LTM-D	5223	5.8	5.9
GAN-30W-G2	LTM-W	2748	5.7	5.9
GAN-30W-G2	IC-D	6417	5.8	5.9
GAN-30W-G2	IC-W	8539	5.8	5.9
GAR-30-L1	LTM-D	6565	6.0	6.25
GAR-30-L1	LTM-W	4800	6.1	6.25
GAR-30-L1	IC-D	7267	6.1	6.25
GAR-30-L1	IC-W	4895	6.4	6.25
GAR-30Y-L1	LTM-D	10279	6.1	6.25
GAR-30Y-L1	LTM-W	9958	6.9	6.25
GAR-30Y-L1	IC-D	10362	6.2	6.25
GAR-30Y-L1	IC-W	11450	6.2	6.25
MS1-20-C	LTM-D	3213	4.2	4.5
MS1-20-C	LTM-W	6647	4.0	4.5
MS1-20-C	IC-D	5423	4.0	4.5
MS1-20-C	IC-W	4937	4.3	4.5

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TABLE 8. EXTRACTED BINDER VISCOSITIES (CONCLUDED).

SAMPLE	TEST AND TREATMENT METHOD	VISCOSITY AT 140°F, POISES	% EXTRACTED BINDER	% DESIGN BINDER
MS2-20-C	LTM-D	4824	4.4	4.5
MS2-20-C	LTM-W	5952	4.4	4.5
MS2-20-C	IC-D	5000	5.3	4.5
MS2-20-C	IC-W	5585	4.3	4.5
MS2-20X-C	LTM-D	4196	4.4	4.5
MS2-20X-C	LTM-W	4256	4.4	4.5
MS2-20X-C	IC-D	4450	4.2	4.5
MS2-20X-C	IC-W	5038	4.2	4.5
UT-10-L2	LTM-D	2331	3.7	3.8
UT-10-L2	LTM-W	2791	3.5	3.8
UT-10-L2	IC-D	2654	3.8	3.8
UT-10-L2	IC-W	4931	3.8	3.8
UT-10Z-L2	LTM-D	3818	3.1	3.8
UT-10Z-L2	LTM-W	4424	4.9	3.8
UT-10Z-L2	IC-D	NOT TESTED	3.6	3.8
UT-10Z-L2	IC-W	5970	3.7	3.8

LTM-D = Lottman-Dry
LTM-W = Lottman-Wet
IC-D = Immersion Compression-Dry
IC-W = Immersion Compression-Wet

TABLE 9. CLAY-GEL COMPOSITION OF EXTRACTED BINDERS FROM DRY AND WET COMPACTED MIXTURES

SAMPLE	TEST AND TREATMENT METHOD	% ASPHALTENES	% SATURATES	% AROMATICS	% POLARS
GAK-30-G1	LTM-D	29.81	7.21	20.21	42.77
GAK-30-G1	LTM-W	29.00	7.36	20.95	42.69
CHANGE	---	0.81	-0.15	-0.74	0.08
GAK-30-G1	IC-D	30.63	7.20	21.86	40.31
GAK-30-G1	IC-W	31.45	7.90	22.27	38.38
CHANGE	---	-0.82	-0.70	-0.41	1.93
GAK-30W-G1	LTM-D	33.25	7.89	18.06	40.80
GAK-30W-G1	LTM-W	33.01	8.70	21.14	37.15
CHANGE	---	0.24	-0.81	-3.35	3.65
GAK-30W-G1	IC-D	32.38	7.36	19.22	41.04
GAK-30W-G1	IC-W	35.57	8.66	18.17	37.60
CHANGE	---	-3.19	-1.30	1.05	3.44
GAG-30-G1	LTM-D	31.94	7.89	20.71	39.45
GAG-30-G1	LTM-W	33.08	7.63	20.23	39.07
CHANGE	---	-1.14	0.26	0.48	0.38
GAG-30-G1	IC-D	32.54	7.79	20.13	39.54
GAG-30-G1	IC-W	31.98	7.74	20.15	40.13
CHANGE	---	0.56	0.05	-0.02	-0.59
GAG-30W-G1	LTM-D	32.76	7.52	19.15	40.57
GAG-30W-G1	LTM-W	34.75	8.21	17.18	39.86
CHANGE	---	-1.99	-0.69	1.97	0.71
GAG-30W-G1	IC-D	35.14	8.77	17.75	38.35
GAG-30W-G1	IC-W	35.36	7.26	17.89	39.48
CHANGE	---	-0.22	1.51	-0.14	-1.13
GAN-30-G2	LTM-D	31.58	7.89	20.97	39.56
GAN-30-G2	LTM-W	31.45	8.31	21.86	38.38
CHANGE	---	0.13	-0.42	-0.89	1.18
GAN-30-G2	IC-D	32.48	7.49	21.66	38.36
GAN-30-G2	IC-W	32.10	7.81	20.06	40.03
CHANGE	---	0.38	-0.32	0.60	-1.67
GAN-30W-G2	LTM-D	34.64	8.47	17.73	39.14
GAN-30W-G2	LTM-W	31.64	7.68	16.78	43.90
CHANGE	---	3.00	0.79	0.95	4.76

TABLE 9. CLAY-GEL COMPOSITION OF EXTRACTED BINDERS
FROM DRY AND WET COMPACTED MIXTURES (CONTINUED).

SAMPLE	TEST AND TREATMENT METHOD	% ASPHALTENES	% SATURATES	% AROMATICS	% POLARS
GAN-30W-G2	IC-D	32.46	7.96	19.55	40.03
GAN-30W-G2	IC-W	32.90	8.65	15.12	43.27
CHANGE	---	-0.50	-0.69	4.43	-3.24
GAR-30-L1	LTM-D	31.71	8.48	20.32	39.48
GAR-30-L1	LTM-W	30.99	7.57	20.25	41.17
CHANGE	---	0.72	0.91	0.07	-1.69
GAR-30-L1	IC-D	30.60	7.16	21.27	40.96
GAR-30-L1	IC-W	31.91	7.49	20.54	39.83
CHANGE	---	-1.31	-0.33	0.73	1.13
GAR-30Y-L1	LTM-D	33.26	8.19	20.03	38.52
GAR-30Y-L1	LTM-W	34.16	7.45	17.69	40.70
CHANGE	---	-0.90	0.74	2.34	2.18
GAR-30Y-L1	IC-D	34.38	8.43	18.39	38.80
GAR-30Y-L1	IC-W	34.82	8.14	17.74	39.30
CHANGE	---	-0.44	0.29	0.65	-0.50
UT-10-L2	LTM-D	27.77	12.40	21.69	38.14
UT-10-L2	LTM-W	27.94	12.65	21.31	38.10
CHANGE	---	-0.17	-0.25	0.38	0.04
UT-10-L2	IC-D	28.80	13.02	20.20	37.98
UT-10-L2	IC-W	29.96	12.90	20.58	36.57
CHANGE	---	-1.16	0.12	-0.38	1.41
UT-10Z-L2	LTM-D	27.82	13.95	21.78	36.45
UT-10Z-L2	LTM-W	28.72	13.74	21.00	36.54
CHANGE	---	-0.90	0.21	0.78	-0.09
UT-10Z-L2	IC-D	26.84	13.59	19.30	40.27
UT-10Z-L2	IC-W	28.93	14.00	19.80	37.26
CHANGE	---	-2.09	-0.41	-0.50	3.01
MS1-20-C	LTM-D	31.08	13.10	22.02	33.08
MS1-20-C	LTM-W	30.80	10.07	27.56	31.57
CHANGE	---	0.28	3.03	-5.54	2.23
MS1-20-C	IC-D	32.79	11.38	22.04	33.82
MS1-20-C	IC-W	33.19	11.28	21.88	33.65
CHANGE	---	-0.40	0.10	0.16	0.17

TABLE 9. CLAY-GEL COMPOSITION OF EXTRACTED BINDERS
FROM DRY AND WET COMPACTED MIXTURES (CONCLUDED).

SAMPLE	TEST AND TREATMENT METHOD	% ASPHALTENES	% SATURATES	% AROMATICS	% POLARS
MS2-20-C	LTM-D	33.84	12.83	20.76	32.57
MS2-20-C	LTM-W	34.7.	11.11	20.44	33.71
CHANGE	---	-0.90	1.72	0.32	-1.14
MS2-20-C	IC-D	32.83	12.56	20.63	33.98
MS2-20-C	IC-W	34.13	13.10	18.77	33.99
CHANGE	---	-1.30	-0.54	1.86	-0.01
MS2-20X-C	LTM-D	33.15	13.37	20.02	33.46
MS2-20X-C	LTM-W	33.55	13.67	19.34	33.44
CHANGE	---	-0.40	-0.30	0.68	0.02
MS2-20X-C	IC-D	33.39	11.71	20.40	34.50
MS2-20X-C	IC-W	33.56	12.08	19.55	34.81
CHANGE	---	-0.17	-0.37	0.85	-0.31

LTM-D = Lottman-Dry

LTM-W = Lottman-Wet

IC-D = Immersion Compression-Dry

IC-W = Immersion Compression-Wet

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TABLE 10. FUNCTIONAL GROUP ANALYSIS[a] FOR SELECTED EXTRACTED
BINDERS AND THEIR CLAY-GEL POLAR FRACTIONS
FROM DRY AND WET COMPACTED MIXTURES.

| SAMPLE | TEST AND TREATMENT METHOD | KETONES[b] | CARBOXYLATES | | SULFOXIDES[e] |
			FREE[c]	SALTS[d]	
GAR-30-L1	LTM-D	TRACE	0.011	0	0.05
GAR-30-L1	LTM-W	TRACE	0.005	0	0.05
CHANGE	---	---	0.006	0	0
GAR-30-L1	IC-D	TRACE	0.014	0	0.05
GAR-30-L1	IC-W	0.02	0.007	0.007	0.05
CHANGE	---	---	0.007	-0.007	0
GAR-30-L1-POLAR	LTM-D	0.15	0.018	0	0.23
GAR-30-L1-POLAR	LTM-W	0.19	0	0	0.17
CHANGE	---	-0.04	0.018	0	0.05
GAR-30-L1-POLAR	IC-D	0.17	0.016	0	0.20
GAR-30-L1-POLAR	IC-W	0.15	0.018	0	0.24
CHANGE	---	0.02	-0.002	0	-0.04
MS1-20-C	LTM-D	0.09	0	0	0.14
MS1-20-C	LTM-W	0.09	TRACE	0	0.14
CHANGE	---	0	---	0	0
MS1-20-C	IC-D	0.07	TRACE	0	0.14
MS1-20-C	IC-W	0.07	<0.01	0	0.18
CHANGE	---	0	---	0	-0.04
MS1-20-C-POLAR	LTM-D	0.22	0	0	0.30
MS1-20-C-POLAR	LTM-W	0.24	0	0	0.29
CHANGE	---	-0.02	0	0	-0.01
MS1-20-C-POLAR	IC-D	0.19	0.005	0	0.30
MS1-20-C-POLAR	IC-W	0.24	<0.01	0	0.30
CHANGE	---	-0.05	---	0	0
MS2-20-C	LTM-D	0.05	TRACE	0	0.16
MS2-20-C	LTM-W	0.07	TRACE	0	0.18
CHANGE	---	-0.02	---	0	-0.02

TABLE 10.   FUNCTIONAL GROUP ANALYSIS[a] FOR SELECTED EXTRACTED
            BINDERS AND THEIR CLAY-GEL POLAR FRACTIONS
            FROM DRY AND WET COMPACTED MIXTURES (CONCLUDED).

| SAMPLE | TEST AND TREATMENT METHOD | KETONES[b] | CARBOXYLATES | | SULFOXIDES[e] |
			FREE[c]	SALTS[d]	
MS2-20-C	IC-D	TRACE	TRACE	0	0.30
MS2-20-C	IC-W	0.04	0	0	0.28
CHANGE	---	---	---	0	0.02
MS2-20-C-POLAR	LTM-D	0.18	0.005	0	0.30
MS2-20-C-POLAR	LTM-W	0.18	TRACE	0	0.28
CHANGE	---	0	---	0	0.02
MS2-20-C-POLAR	IC-D	0.14	TRACE	0	0.29
MS2-20-C-POLAR	IC-W	0.14	0	0	0.30
CHANGE	---	0	0	0	-0.01

Note: All concentrations are in moles/liter.

        a - Anhydrides not included due to ester impurities
        b - Ketones +/- 0.02, change +/- 0.03
        c - Carboxylic acids +/- 0.005
        d - Carboxylate salts determined by difference;
            thus error > +/- 0.005
        e - Sulfoxides +/- 0.02, change +/- 0.03

        LTM-D = Lottman-Dry
        LTM-W = Lottman-Wet
        IC-D = Immersion Compression-Dry
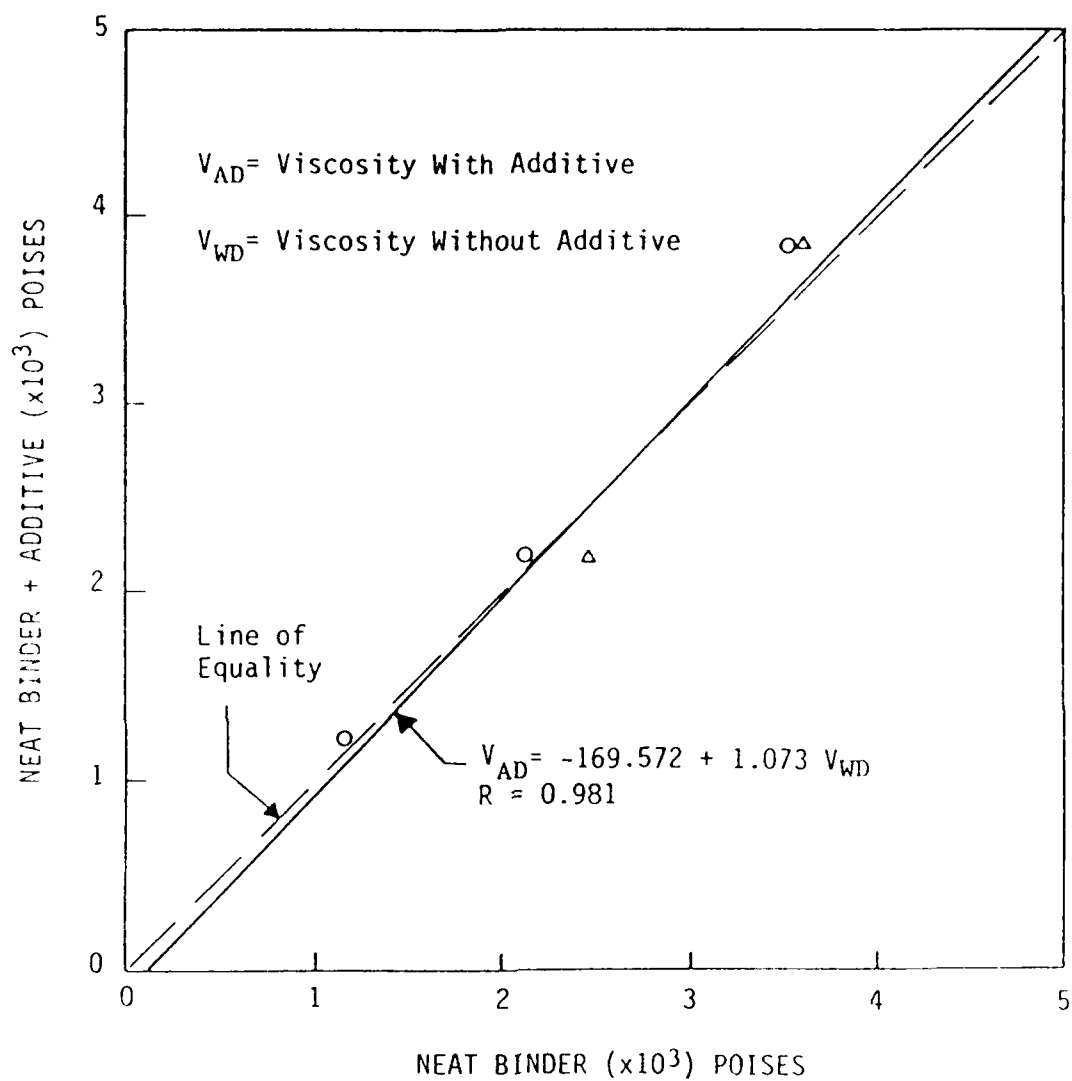   IC-W = Immersion Compression-Wet

Figure 2.   Comparing Binder Viscosity (140°F)
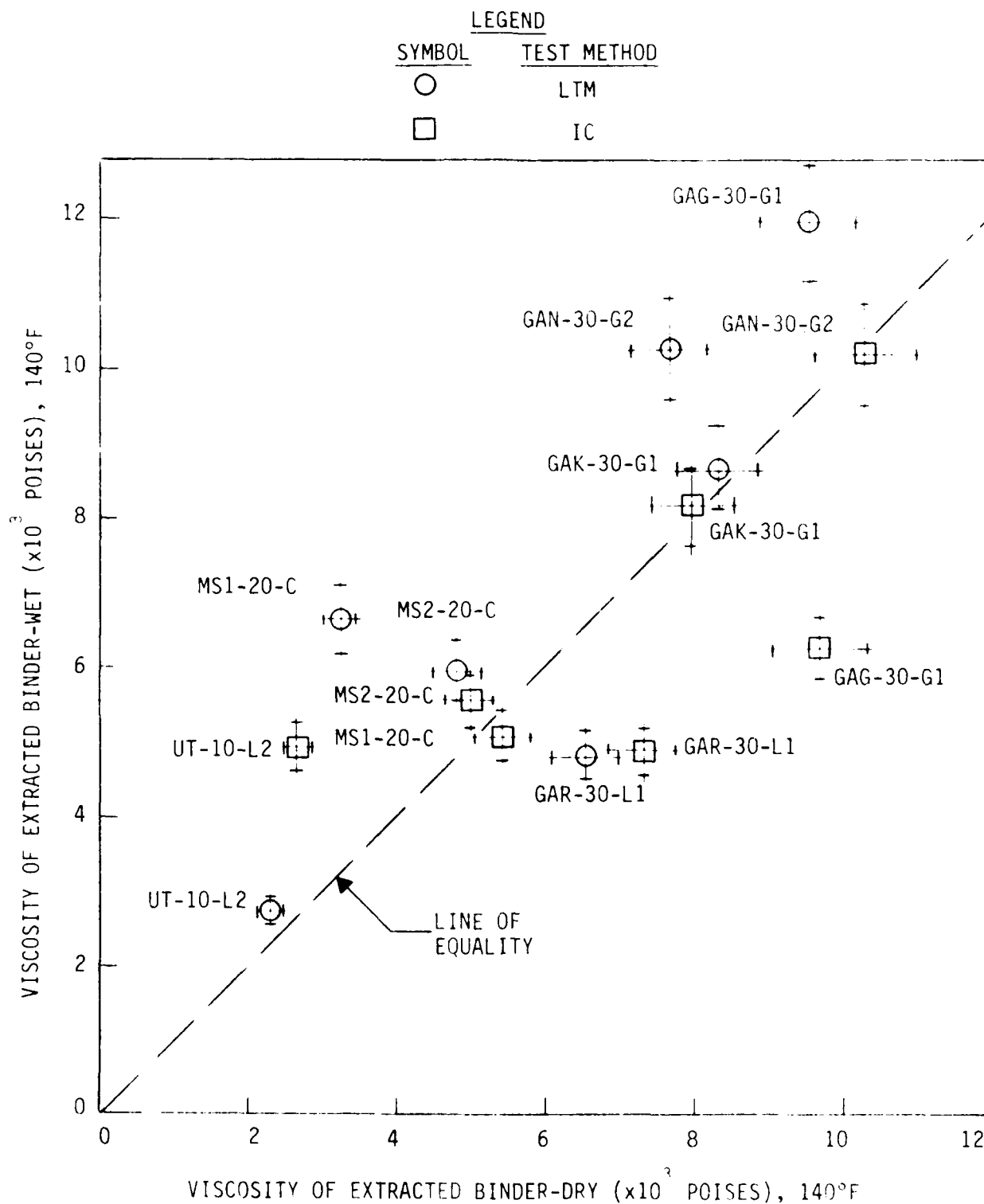   With/Without Additives (Tables 3 and 5).

Figure 3. Comparing Extracted Viscosities for Water-Treated
and Dry Mixtures (Without Additives).

mixtures without additives. Each point includes a pair of mean viscosity values and approximate precision limits (D2S %) of 6.5 percent as defined in standard ASTM D-2872 (Reference 31). The results in this figure indicate that the viscosity values of binders from LTM moisture-conditioned mixtures may exceed those of binders from dry LTM mixtures. The converse seems to hold for IC mixtures. However, the statistical significance of the pattern observed in this figure cannot be determined because of such confounding factors as variation of aggregate types and binder grades. In some systems, there is softening which could possibly be due to trace recovery solvents or action of water molecules which could be occluded in binder material. Discussions with other researchers revealed that binders will plasticize and soften in the presence of water. Table 8 also lists percent recovered binder content and design percent binder content. The level of recovered binder content is within the general precision limits of design and/or extraction values of ±0.5 percent (Reference 31).

Material Properties

The results for the mixtures listed in Tables 6 and 7 are further summarized in Tables 11 and 12. Table 11 lists results of percent retained strength, use or no use of additive, and percent saturation. Table 12 lists indices which have been defined in terms of properties measured by the IC and LTM procedures. Thus, the underlying discussion will be primarily based on the results in Tables 11 and 12.

1. The relative core gravity (RCG) is defined as the ratio between the IC bulk specific gravity and the LTM bulk specific gravity. This indicates that LTM mixtures are more dense than the IC mixtures by 2 to 4 percent (3 to 5 PCF), and implies that the LTM mixes would be less penetrable by water than the IC mixtures using the same treatment procedure. Mixes with additives have higher RCG values than nontreated mixes. This is due to increased density of the additive-modified mix. This density increase may be partially responsible for the decrease in water damage observed in the IC mixtures with additives, as measured by the percent retained strength. However, due to confounded variables, the effects of additive and density cannot be separated. The bulk specific gravity of the LTM mixtures with additives did not change, but the moisture resistance increased as measured by the percent retained strength.

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TABLE 11. PERCENT RETAINED STRENGTH AND SATURATION DATA (FHWA).

SAMPLE	% RETAINED STRENGTH		ADDITIVE	% SATURATION	
	LTM	IC	USED	LTM	IC
GAR-30-L1	75.2	84.6	NO	79.4	42.9
GAR-30Y-L1	88.0	83.4	YES	75.4	42.0
GAK-30-G1	29.5	60.6	NO	175.0	71.5
GAK-30W-G1	77.8	89.9	YES	105.7	52.3
GAG-30-G1	4.2	19.3	NO	461.1	207.4
GAG-30W-G1	92.5	102.7	YES	82.6	50.2
GAN-30-G2	35.6	73.1	NO	129.0	71.2
GAN-30W-G2	83.0	95.3	YES	89.2	45.1
MS1-20-C	76.1	83.7	NO	138.8	64.3
MS2-20-C	84.8	92.6	NO	115.5	58.1
MS2-20X-C	83.7	99.4	YES	114.9	54.7
UT-10-L2	77.0	55.7	NO	83.1	69.8
UT-10Z-L2	79.1	87.3	YES	85.1	56.7

TABLE 12. SUMMARY OF RELATIVE INDICES OF BITUMINOUS MIXTURE PROPERTIES.

INDEX	GAR-30-L1	GAR-30Y-L1	GAK-30-G1	GAK-30W-G1	GAG-30-G1	GAG-30W-G1	GAN-30-G2	GAN-30W-G2	MS1-20-C	MS2-20-C	MS2-20X-C	UT-10-L2	UT-10Z-L2
RCG	0.96	0.98	0.97	0.98	0.98	0.98	0.97	0.98	0.96	0.96	0.97	0.98	0.98
RAV	1.82	1.56	1.81	1.59	1.66	1.54	1.59	1.56	2.18	1.94	1.84	1.55	1.55
RPS	0.54	0.56	0.41	0.50	0.45	0.61	0.55	0.51	0.46	0.50	0.48	0.67	0.67
RDS	2.78	3.33	2.70	2.86	2.78	2.78	2.78	2.86	2.22	2.04	2.04	3.13	2.86
DRS	1.13	0.96	2.05	1.15	4.83	1.11	2.08	1.15	1.10	1.09	1.19	0.72	1.10
CPRS LTM	12.8		48.3		88.3		47.4			-1.1		2.1	
CPRS IC	-1.2		29.3		83.4		22.2			6.8		31.6	
CDS LTM	-7.7		-2.3		2.1		4.4			-6.5		6.5	
CDS IC	9.5		2.9		4.3		8.6			-7.9		-1.8	

RCG = core specific gravity (IC) / core specific gravity (LTM)
RAV = air voids (IC) / air voids (LTM)
RPS = saturation (IC) / saturation (LTM)
RDS = dry compressive strength (IC) / dry tensile strength (LTM)
DRS = retained strength (IC) / retained strength (LTM)
CPRS = change in retained strength (%)
CDS = change in dry strength (%)

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Thus, the increased moisture resistance of the LTM briquets may be directly attributable to the use of an additive. Figure 4 summarizes the LTM test results in Table 11 by showing that the antistripping effect of each additive is specific. Additive W imparted the greatest increase in moisture damage-resistance compared to Additives X, Y, and Z in the system under discussion.

2. The percent air voids of all IC mixtures exceed air voids in LTM mixtures. The air voids range from 5.4 to 7.2 percent for IC and 3.3 to 4.3 percent for LTM. Thus, IC-designed mixtures should be more susceptible to moisture damage because of lower densities coupled with high air voids. This observation could not be verified in this study because the LTM and IC mixtures were subjected to different water treatment methods.

3. IC mixtures with additives (Table 6) show reduced percent air voids compared to the unmodified mixtures. This trend agrees with increased density as described in Item 1 above and with increased moisture damage resistance as measured by percent retained strength. These data are summarized in Table 11. The percent air voids did not change in LTM mixtures with additives as observed in IC mixtures. Therefore, it is difficult to attribute the increased moisture damage-resistance in IC mixtures with additives as being solely caused by an additive.

4. In Table 11, 7 of the 13 LTM mixtures are associated with saturation levels exceeding 100 percent compared to 1 of 13 IC mixtures. This observation is congruent with findings of many investigators who have applied the LTM procedure along with other methods (References 10, 26, and 28). The results in Table 11 further indicate that mixtures with additives have a lesser degree of saturation. Figure 5 summarizes the results in Table 11 in terms of percent retained strength, mixture type, and the two test procedures. The plotted results in Figure 5 consist of mixtures which are saturated to less tnan 100 percent.

The percent retained strength of all LTM mixtures listed in Figure 5 exceed the 70 percent minimum suggested by Lottman (Reference 17). This result implies that these mixtures would be considered to be moisture-damage resistant. All IC mixtures but one pass the 70 percent threshold. Finally, the percent retained strength by the IC procedure is higher in four of the six mixtures than corresponding values determined by the LTM procedure. The reason
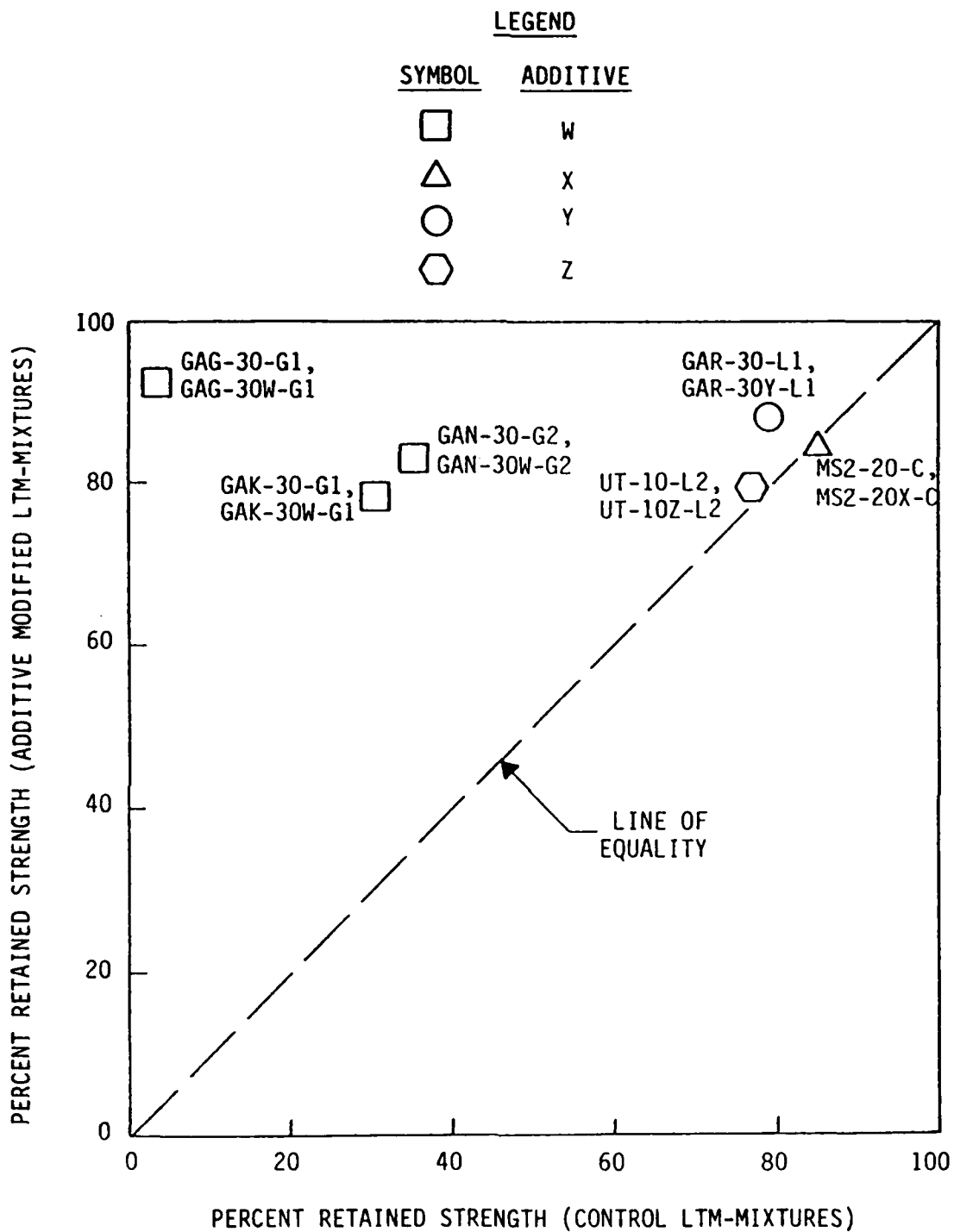
Figure 4. Comparing Percent Retained Strength of Modified
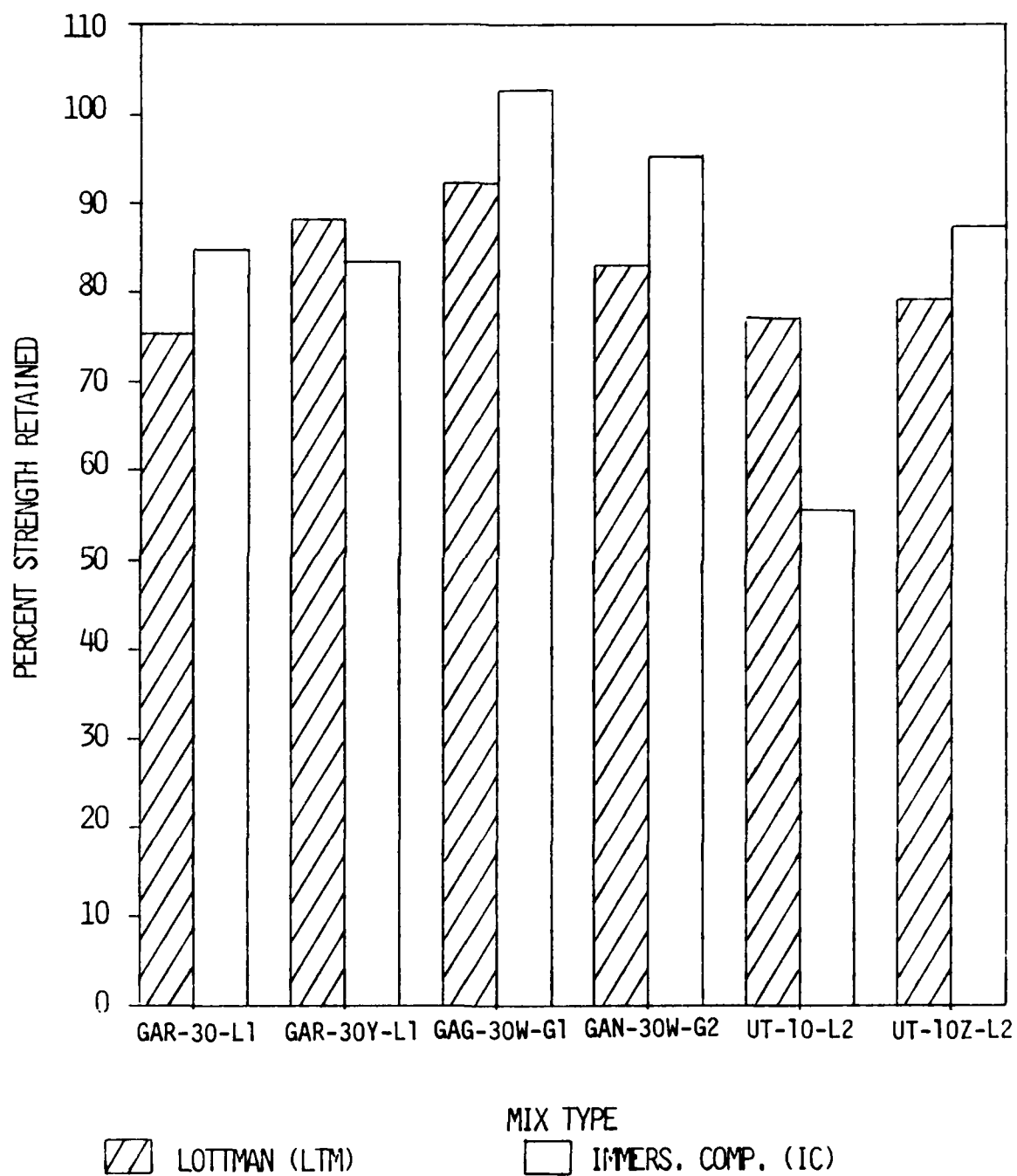and Control LTM-Mixtures (Table 11).

Figure 5. Effect of Test Procedure on Percent Retained Strength
of Bituminous Mixtures.

for this result is not clear, however, the saturation levels in the LTM mixtures are nearly twice the levels in corresponding IC mixtures. This measure of relative percent saturation (RPS) is defined and summarized in Table 12.

The remaining discussion will feature the balance of the parameters listed and defined in Table 12. These include the relative dry strength ratio (RDS), degree of relative severity (DRS), change in percent retained strength (CPRS), and change in dry strength (CDS). Each of these parameters will be discussed below.

RDS is the ratio of dry compressive strength (IC) to dry tensile strength (LTM) of each of the mixtures listed in Table 12. This parameter generally tended to increase with the use of an additive. However, in one case, the RDS parameter remained unchanged, and in another, it decreased. The relationship of RDS to moisture damage is not clearly discernible from the test results.

DRS is redefined as follows:

$$DRS = \frac{Percent\ retained\ strength\ (IC)}{Percent\ retained\ strength\ (LTM)}$$

This index was established to relate the water damage prediction values determined by the IC procedure to those by the more severe LTM procedure. The values of the DRS index in Table 12 vary from 0.72 to 4.83. As DRS approaches unity, the implication is that both IC and LTM procedures are measuring equivalent effects of water on the test specimens. When the index drops below unity, the result implies that the IC procedure causes greater damage than the LTM procedure. When DRS exceeds unity, the LTM procedure has caused more damage than the IC procedure. The DRS index for additive-modified mixtures in Table 12 varied from 0.96 to 1.15. Thus, for the additive-modified mixtures in this study, the data suggest that LTM and IC procedures measure equally the moisture effects on the test specimens, unlike the unmodified mixtures.

Changes in percent retained strength (CPRS) is the numerical difference for a partiular material between the additive- and nonadditive-modified mixtures. This parameter generally increased due to the addition of an additive. This observation implies increased moisture resistance of mixtures in the presence of the particular additives used in this study. However, in the

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IC mixture of GAR-30Y-L1 type, the effect of Additive Y resulted in a very slight decrease in moisture resistance. Since no error limits have been established for percent retained strength, this slight decrease may be due to random error.

Finally, CDS is defined as the change in the dry strength between additive- and non-additive-modified mixtures expressed as a percentage of dry strength in the unmodified condition. The results in Table 12 indicate that 50 percent of LTM additive-modified mixtures decreased in dry strength in comparison to about 16 percent for IC mixtures. A relationship between CDS and CPRS data from Table 12 is presented in Figure 6. The results in this figure indicate that the smaller the change in CDS, the higher the percent change in retained strength. Thus, a small change in CDS may be indicative of improved moisture-damage resistance when additives are used. This was the case in this study for LTM and IC procedures.

In summary, using the LTM (Reference 17) guideline of 70 percent retained strength, all mixtures with additives in this study would be classified as moisture-damage resistant. The LTM procedure can produce mixtures with saturation levels exceeding 100 percent, a condition which may damage the structural integrity of the specimens. LTM mixtures are slightly denser than IC mixtures, however, in the presence of additives, such as the ones used in this study, the two test procedures can produce equally dense mixtures. This property can increase moisture-damage resistance. Similarly, high void content can be expected to decrease moisture resistance of bituminous mixtures. The use of the additives in this study can enhance the percent retained strength and, in turn, improve the moisture resistance of mixtures as defined by these test procedures. The data in this study were used to define an index of relative severity which can be used to rate various methods used in evaluating the degree of moisture damage. The results show that when additives are present, the LTM and IC procedures may equally predict the degree of moisture damage. When additives are removed, results of LTM and IC are dramatically different.

Chemical Considerations

The Clay-Gel composition of virgin asphalts obtained from FHWA is presented in Table 3. Asphalt B-5851 has a higher percentage of asphaltenes, saturates, and aromatics but a smaller amount of polars than B-5856. This is
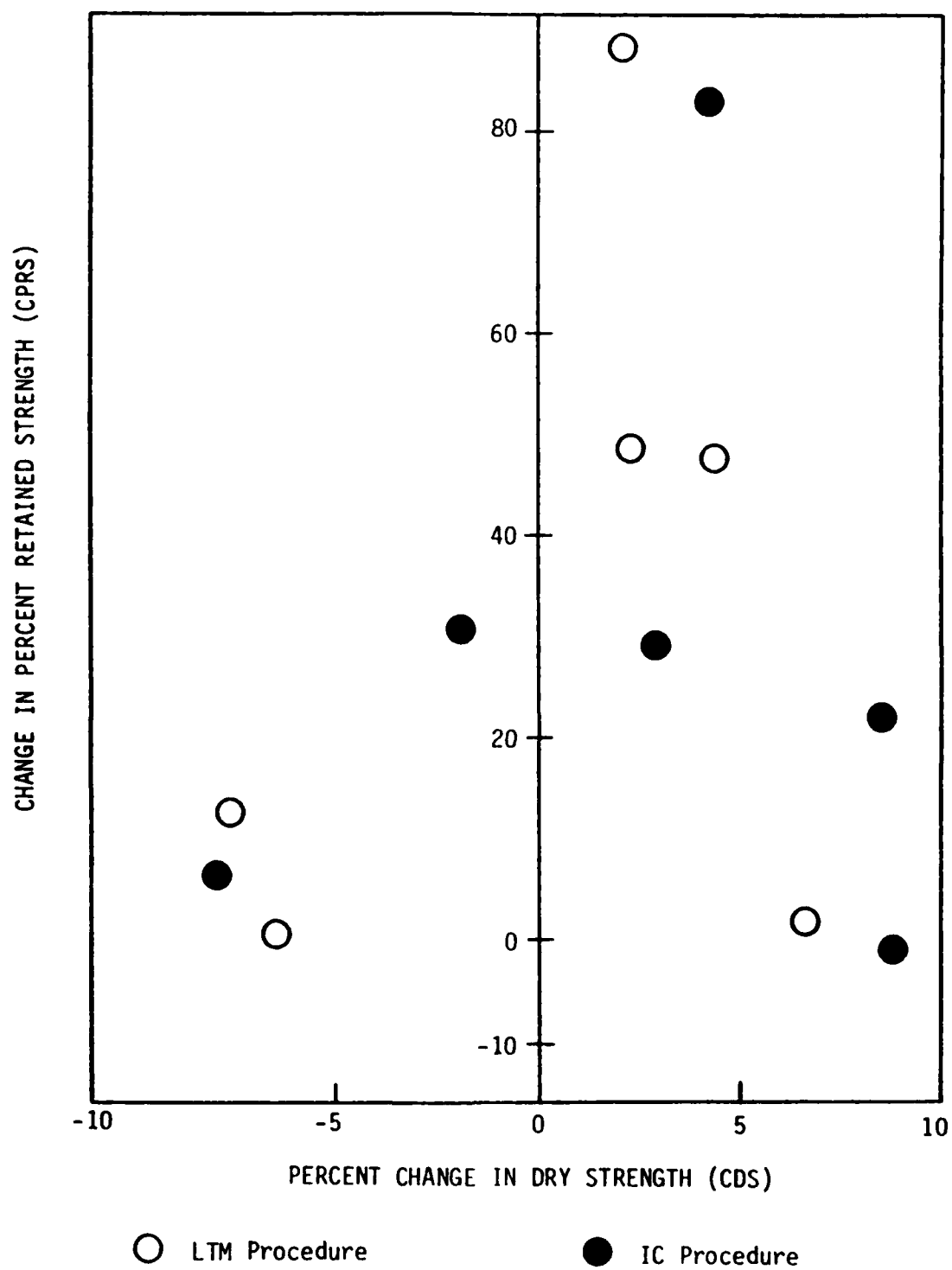
Figure 6. Change in Percent Retained Strength (CPRS) versus
Percent Change in Dry Strength (CDS) (Table 12).

reflected in the infrared analysis shown in Table 4. B-5856 has a larger total
concentration of polar functionalities and much greater quantities of carbox-
ylic acids than B-5851. The use of additives X and Y in B-5851 and 5856,
respectively, cause an increase in the asphaltene fraction at the expense of
both the saturate and aromatic fraction. The increase observed in the polar
fractions in both cases are with NMERI's precision limits, thus,this increase
may be due to experimental error.

Clay-Gel data for binders extracted from wet and dry compacted mixtures
are given in Table 9. Although the differences of the asphaltenes and polar
fractions between wet and dry samples appear to be random for mixtures without
additives, there were general trends observed in the changes occurring in the
saturate and aromatic fractions. In Figure 7, the percent retained strength
(PRS) is plotted as a function of the change in saturate fraction. In general,
mixtures which show decreases in the amount of saturates between wet and dry
conditions have higher PRS values. The opposite effect is noted for the aro-
matic fraction, as shown in Figure 8. If the amount of aromatics increases
after water treatment, the PRS value is generally higher. Although the magni-
tude of some of the changes occuring between wet and dry specimens fall within
the NMERI in-house precision limits, these points follow the trend of data
points lying outside the precision limits and are considered to be valid.
If the data base was larger, more definite trends may be observed. In both
Figures 7 and 8, all points with percent water saturation values exceeding
100 percent are labelled. It is interesting to note that, in general, these
data are not consistent with data having percent water saturation values less
than 100 percent.

The IR data are limited to select samples. However, there are some obser-
vations to be made. The concentration of ketones in the GAR-30-L1 whole
extracted binder was detectable only in trace amounts, but in the polar Clay-
Gel fraction, an increase in concentration occurs during water treatment as
shown in Figure 9. No detectable changes were evident in the sulfoxide concen-
tration for the GAR-30-L1 whole extracted binder. In the polar GAR-30-L1 frac-
tion, a decrease in sulfoxide concentration occurred in the LTM wet sample and
an increase in the IC wet specimen (Figure 9). In the MS1-20-C and MS2-20-C
systems, the ketone concentration either remained the same, or increased after
water treatment (Figure 10). This same observation was noted for the sulfoxide
concentration with two exceptions, the polar fractions of LTM samples MS1-20-C
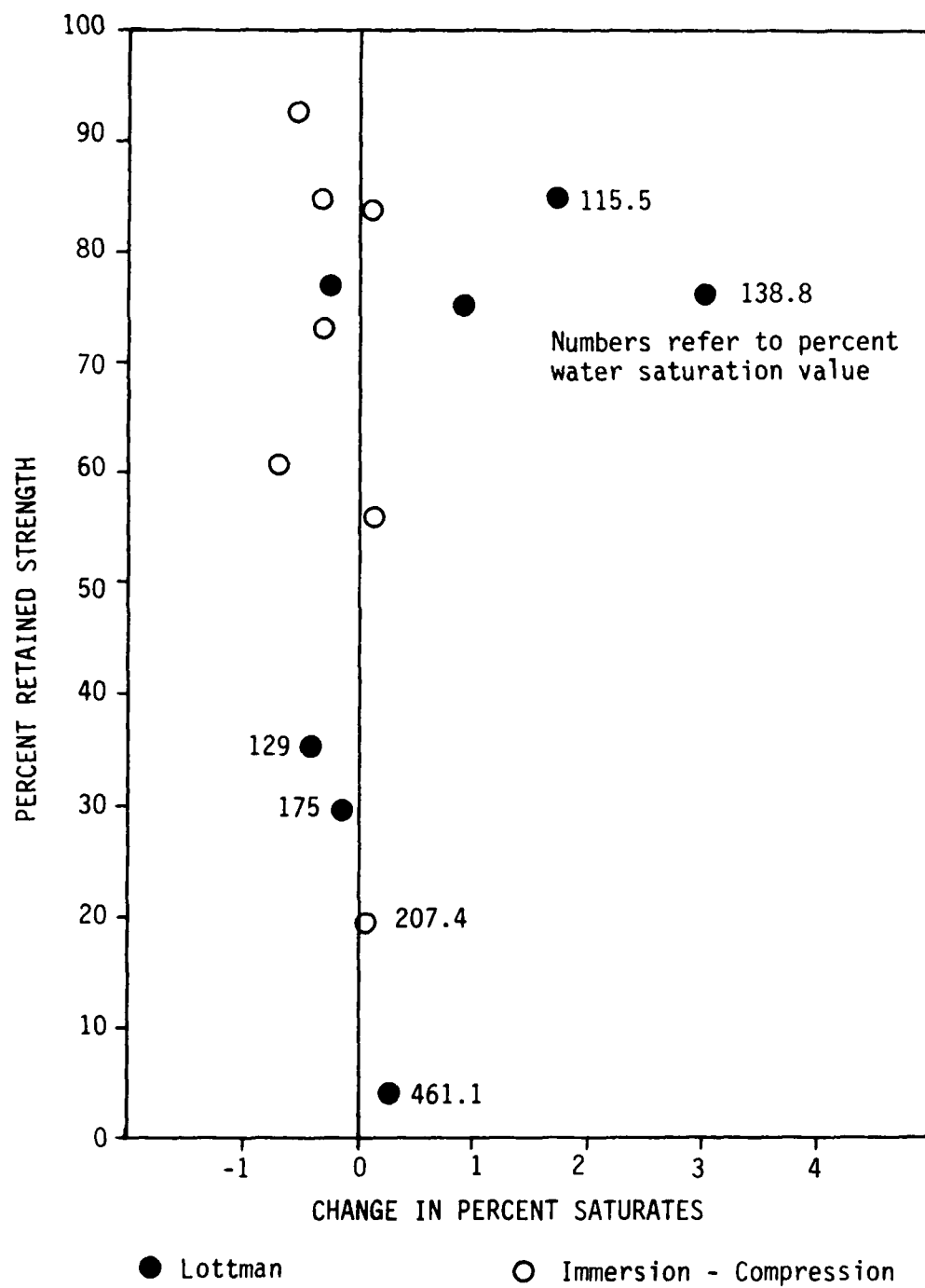
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Figure 7.   Percent Retained Strength Versus Change in
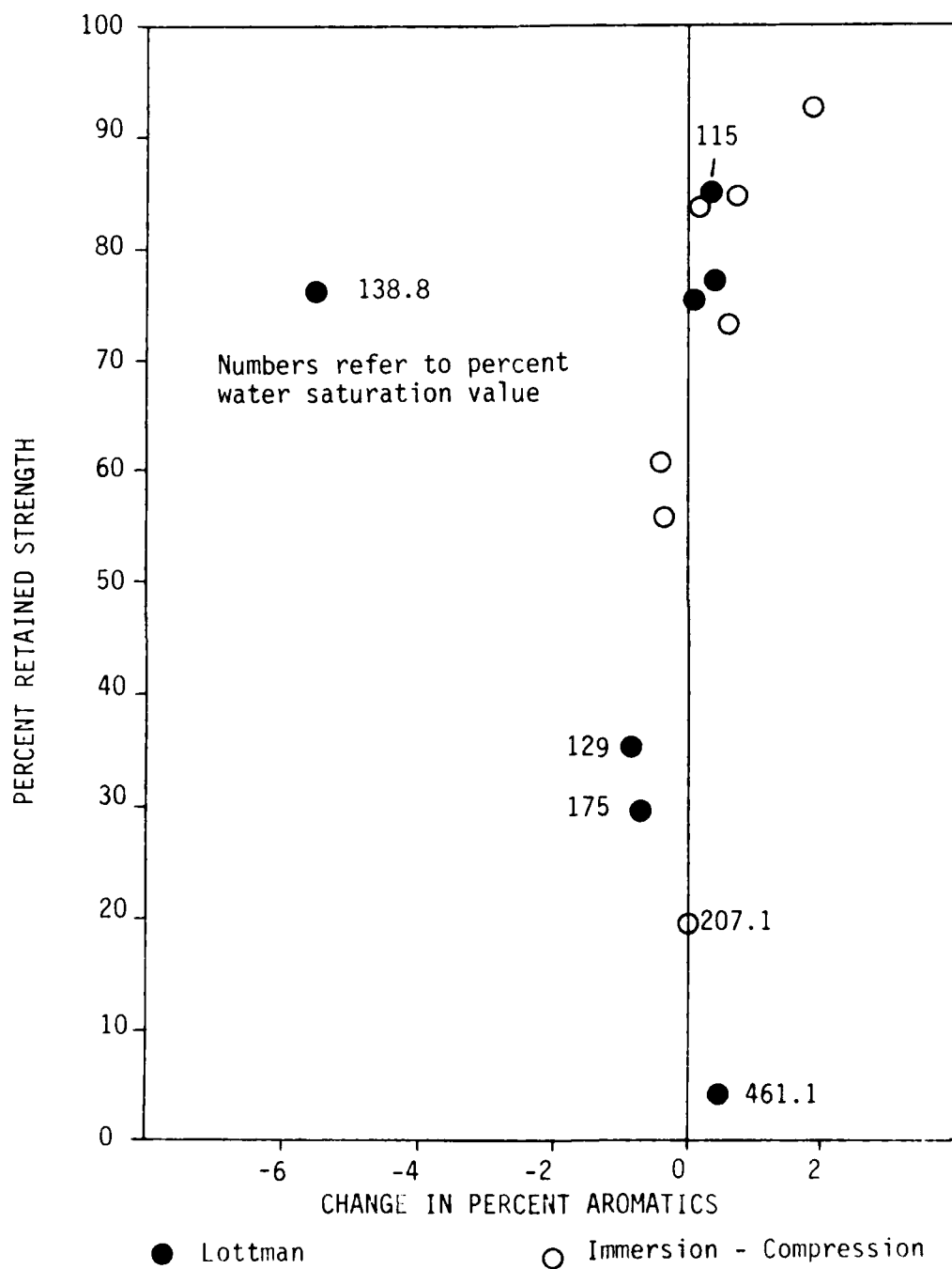   Percent Saturates.

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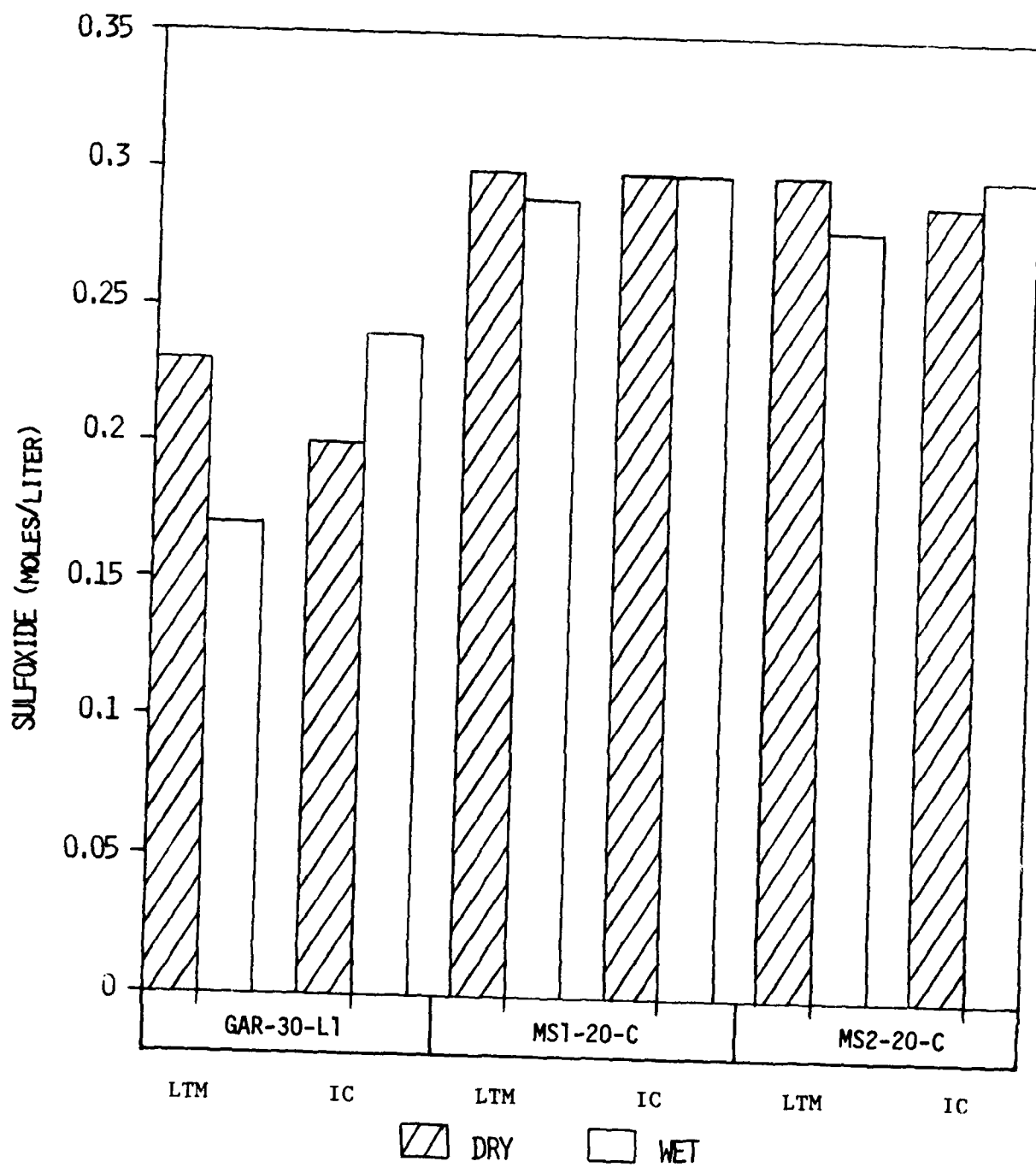Figure 8.   Percent Retained Strength Versus Change in
Percent Aromatics.

Figure 9. Changes in Sulfoxide Concentrations from Dry to Wet
for Lottman and Immersion-Compression Mixtures.

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and MS2-20-C as shown in Figure 10. Note that these were the only samples having percent water saturation values greater than 100 (138.8 and 115.5 for MS1-20-C and MS2-20-C, respectively). The increase in concentrations reported here may be from increased oxidation of the mixes subjected to water treatment. This hypothesis is supported by the increase in viscosity of extracted binders from water-treated mixtures. The carboxylic acid data were not included in this discussion because of inconsistencies in the concentrations.

In summary, changes in the aromatic and saturate fractions occuring upon water treatment of mixtures containing no additives seem to follow opposing trends. No such trends were observed in additive-modified mixtures. The viscosity and IR data indicate that oxidation may be enhanced in mixtures subjected to water treatment. A detailed explanation of why these trends occur, and the apparent anomalies caused by saturation levels of compacted mixtures exceeding 100 percent is not evident at this time.

Proposed Model Relationship

The results of this study were proposed to fit a generalized statistical model relating a measure of performance (PRS) to mixture and binder properties. The proposed model is:

Percent Retained Strength (PRS) = f (binder grade, saturates, asphalt-
enes, aromatics, polars, air voids,
binder content, density, saturation,
etc.).

The model was tested using a multivariant regression statistical analysis program. Binder and mixture properties before and after water treatment showed no correlation with PRS. The lack of correlations may be due to insufficient data from one test procedure compounded by the differences in aggregate type without consistent asphalt grade variations.

To test the proposed model, a large data base, unavailable in this study and preferably obtained by the same test procedure, would be required. The results of such a model analysis may indicate which mixture and binder properties significantly influence the PRS and in what order. The information gained from such a relationship may be useful in material selections and in mix design methodologies.
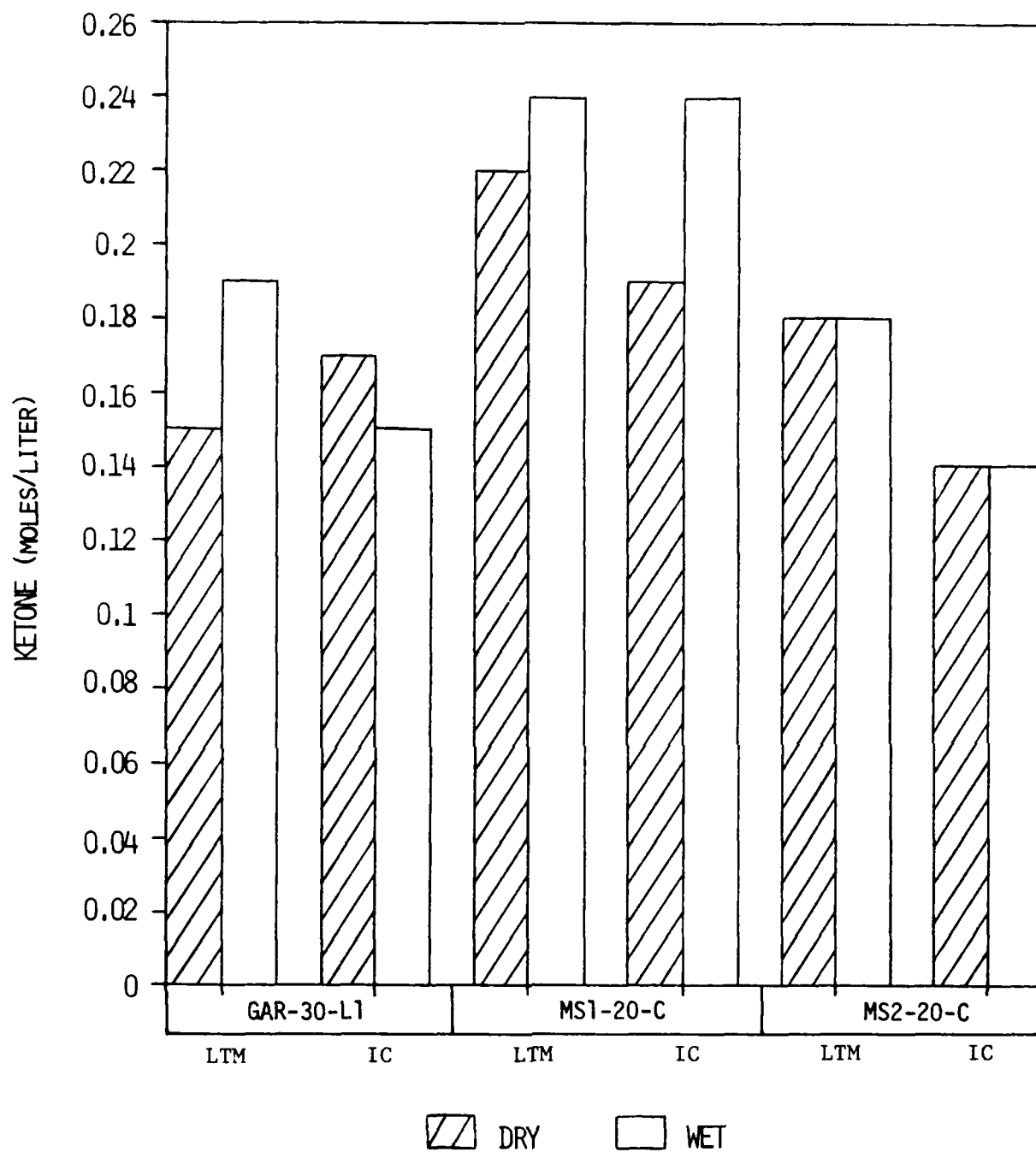
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Figure 10 Changes in Ketone Concentration from Dry to Wet for
Lottman and Immersion-Compression Mixtures.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Additives used in this study increased retained strength of compacted asphalt-concrete test specimens.

2. High air voids increase water susceptibility.

3. Test specimens containing additives used in this study achieved similar values for retained strength in both Lottman and immersion compression tests, i.e., both tests appear to have similar severity.

4. Higher retained strengths were observed for immersion compression results than for Lottman tests when specimens contained no additives, i.e., Lottman appears more severe.

5. All mixtures containing additives in this study achieved at least 70 percent retained strength when evaluated by the Lottman procedure.

6. An Index of Relative Damage defined in this study may be useful in judging relative differences between water-damage tests.

7. Oxidation may be accelerated due to the presence of water as measured by increased viscosity, ketones, and sulfoxides.

8. Water treatment may affect the aromatic and saturate fractions.

9. A decrease in saturate fraction may suggest increased retained strength. The opposite trend is observed in the aromatic fraction. However, the data available were insufficient to soundly define a relationship.

10. A statistical relationship was not found to exist between percent retained strength, mixture properties, and binder composition fractions. The data available were inadequate to define a relationship.

RECOMMENDATIONS

The following list of recommendations was derived from this research:

1. Mixtures containing additives demonstrate enhanced performance over mixtures without additives as measured by laboratory methods. Field performance studies would supply information on long-term performance of mixtures containing additives.

2. Limiting the air voids would reduce the oxidation potential and ability of water to permeate the asphalt-aggregate mixture.

For further study:

1. Limit the variability of test parameters by defining specific ranges for compacted mixture density, air voids, and percent water saturation values. Water saturation should not exceed 100 percent.

2. One specific design should be chosen and used throughout the study. For example, to study the effect of water on the binder in paving mixtures, the use of one aggregate would be advantageous to eliminate the various catalytic activities of different aggregates.

3. A model relationship between retained strength and mixture physical and binder composition properties may be developed, provided adequate data are obtained. These data should represent various levels of mixture and binder grade properties, and should be generated by one test procedure with strict testing controls.

4. If additives are to be used, infrared analysis of mixtures with additives should be included.

5. Samples should be tested in individual water baths without changing the water for the duration of that test. The water should be analyzed for possible aromatic content by ultraviolet and/or NMR spectroscopy. Functional group analysis could be accomplished by IR. Elemental analysis would yield the percent carbon, nitrogen, and sulfur in the water. Atomic absorption spectroscopy could be used to detect metal ions in the water, especially if mixtures containing additives were studied.

REFERENCES

1. Petersen, J. C., Plancher, H., Ensley, E. K., Venable, R. L., and Miyake, G., "Chemistry of Asphalt-Aggregate Interactions: Relationship with Pavement Moisture-Damage Prediction Test," TRR, No. 843, 1982.

2. Taylor, M. A., and Khosla, N. P., "Stripping of Asphalt Pavements: State of the Art," TRR, No. 911, 1983.

3. Lottman, R. D., "Laboratory Test Method for Predicting Moisture Induced Damage to Asphalt Concrete," TRR, No. 843, 1982.

4. Fromm, H. J., "The Mechanisms of Asphalt Stripping From Aggregate Surfaces," Proceeding, Association of Asphalt Paving Technologists, Vol. 43, 1974, pp. 191-223.

5. Schmidt, R. J., and Graf, P. E., "The Effect of Water on the Resilient Modulus of Asphalt Treated Mixes," Proceedings, Association of Asphalt Paving Technologists, Vol. 41, 1972, pp. 118-162.

6. Majidzadeh, K., and Brovold, F. N., "State of the Art: Effect of Water on Bitumen-Aggregate Mixtures," HRB, Special Report, 1968.

7. Dohaney, W. J., "Stripping Characteristics of Paving Grade Asphalts Used in New Brunswick," Proceedings, Canadian Technical Asphalt Association, Vol. 13, 1968, pp. 267-275.

8. Chehovits, J. G., and Anderson, D. A., "Upgrading of Marginal Aggregates for Improved Water Resistance of Asphalt Concrete," TRR, No. 762, 1980, pp. 46-52.

9. "Symposium on Effects of Water on Bituminous Paving Mixtures", ASTM, Special Technical Publication, No. 240, 1958.

10. Petersen, J. C., Dorrance, S. M., Ensley, E. K., Barbour, F. A., Barbour, R. V., and Haines, W. E., Paving Asphalts: Chemical Composition, Oxidative Weathering and Asphalt-Aggregate Interactions, Part II, Interim Report, No. FHWA-RD-74-71, June, 1974.

11. Petersen, J. C., Ensley, E. K., Plancher, H., and Haines, W. E., Paving Asphalts: Asphalt-Aggregate Interactions and Asphalt Intermolecular Interactions, FHWA-RD-77-25, 1977.

12. Plancher, H., Dorrance, S. M., and Petersen, J. C., "Identification of Chemical Types in Asphalt Strongly Adsorbed at the Asphalt-Aggregate Interface and Their Relative Displacement by Water," Proceedings, Association of Asphalt Paving Technologists, Vol. 46, 1977.

13. Plancher, H., Chow, C., Holmes, S. A., and Petersen, J. C., "Moisture-Induced Damage in Bituminous Pavement--A Study of Nitrogen Compound Interactions with Aggregate," Proceedings of the International Symposium on Progressi Mellc Technologia del Bitumi, San Donato Malanese, Italy, 1981, pp. 263-273.

14. **Symposium on Water Damage of Asphalt Pavements:** Its Effect and Prevention, (To be published), ASTM, December 1984.

15. Tunnicliff, D. G., and Root, R. E., "Antistripping Additives in Asphalt Concrete--State of the Art," **Proceedings, Association of Asphalt Paving Technologists,** Vol. 51, 1982.

16. Maupin Jr., G. W., "Analysis and Repair of Water Damaged Bituminous Pavements," **TRR,** No. 821, 1981, pp. 12-16.

17. Lottman, R. P., Chen, R. P., Kumar, K. S., and Wolf, L. W., "Laboratory Test System for Prediction of Asphalt Concrete Moisture Damage," TRR, No. 515, 1974, pp. 18-26.

18. NCHRP-project 10-17--**Method of Test for Determination of the Effect of Moisture and Antistripping Additives on Asphalt Concrete Paving Mixtures,** Revision 2-10-84.

19. ASTM D-1075-76, "Effect of Water on Cohesion of Compacted Bituminous Mixtures," Volume 04.03, 1985.

20. Plancher, H. et al., "A Simple Laboratory Test to Indicate the Water Susceptibility of Asphalt-Aggregate Mixtures to Moisture Damage During Repeated Freeze-Thaw Cycles," presented at the 1980 Canadian Technical Asphalt Association Meeting in Victoria, B.C., November 24-26, 1980.

21. Kennedy, T. W., McGennis, R. B., and Roberts, F. L., "Investigation of Moisture Damage to Asphalt Concrete and Its Effects on Field Performance- -A Case Study," presented at the 62nd Annual Meeting of the Transportation Research Board, Washington, D.C., January 1983.

22. Kennedy, T. W., Roberts, F. L., and Lee, K. W., **Texas Freeze-Thaw Pedestal Test for Evaluating Moisture Susceptibility for Asphalt Mixtures,** Research Report 253-3, Project 3-9-79-253, Center for Transportation Research, The University of Texas at Austin, August 1981.

23. Kennedy, T. W., Roberts, F. L., and Lee, K. N., "Evaluation of Moisture Susceptibility of Asphalt Mixtures Using the Texas Freeze-Thaw Pedestal Test," **Proceedings, Association of Asphalt Paving Technologists,** Vol. 51, 1982, pp. 327-341.

24. Schrimsher, T. et al., **Selection of Optimum Binder Content for Bituminous Treated Bases,** California Division of Highways, Report No. CA-4Y-MR-3378-1-73-03, January 1973.

25. Goetz, W. H., "Methods of Testing for Water Resistance of Bituminous Paving Mixtures," **ASTM, STP** No. 240, 1958, pp. 84-94.

26. Button, J. W., Rincon-Valdez, R., Epps, J. A., and Little, D. N., **Developmental Work on a Test Procedure to Identify Water Susceptible Asphalt Mixtures,** TTI-2-9-80-287-1, Texas Transportation Institute, 1982.

27. Gilmore, D. W., Lottman, R. P., AND Scherocman, J. A., "Use of Indirect Tension Measurements to Examine the Effect of Additives on Asphalt Concrete Durability," **Proceedings, Association of Asphalt Paving Technologists,** Vol. 53, 1984, pp. 495-524.

28. Tunnicliff, D. G., and Root, R. E., "Testing Asphalt Concrete for Effectiveness of Antistripping Additives," **Proceedings, Association of Asphalt Paving Technologists,** Vol. 52, 1983, pp. 535-560.

29. ASTM D-1559-82, Standard Test Method for Resistance to Plastic Flow of Bituminous Mixtures Using Marshall Apparatus, Vol. 04-03, 1985.

30. ASTM D-1074-83, "Standard Test Method for Compressive Strength of Bituminous Mixtures," Vol. 04-03, 1985.

31. AASHTO T-164-80, "Standard Method of Test for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures," 13th Edition, Part II, 1982, pp. 574-587.

APPENDIX A

MODIFICATIONS TO THE CLAY-GEL
COMPOSITIONAL ANALYSIS, FORMERLY ASTM D-2007-75

The following modifications to the Clay-Gel compositional analysis method were implemented by the New Mexico Engineering Research Institute to improve mass balance and make the method applicable to a variety of asphaltic materials.

In the original ASTM round-robin set of tests, the polars did not exceed 25 percent in each sample, and the saturates were greater than 20 percent. To utilize this method for asphalts, modifications were required to make it compatible with a variety of asphaltic materials with varying percentages of asphaltenes, polars, saturates, and aromatics.

Two modifications were made before NMERI began using this procedure. The first involved stripping the column of aromatics instead of calculating them by difference. The ASTM method calls for calculating the aromatic fraction by difference. If all polars are not recovered from the clay column, there is an erroneous lumping of these polar compounds into the aromatic fraction. This leads to less polar compounds and a much higher aromatic content. A solvent system of 70 percent toluene and 30 percent methanol was used to strip the silica gel column and recover the aromatic fraction.

The second change was made in the calculations. According to the ASTM procedure, if the sample size is 5 grams or less, the calculation for polar compounds is shown below.

$$\text{Percent polars} = 0.88 \times \frac{\text{Grams of polars recorded}}{\text{Grams of total sample}} \times 100$$

The factor of 0.88 was established experimentally to maintain continuity of results over a wide range of polar compounds (taken from the former ASTM D-2007-75). To establish a true mass balance, this factor was eliminated from the calculations.

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The following modifications were incorporated after testing was initiated and problems were encountered. After these modifications were made, the repeatability of the results improved.

AMOUNT OF SOLVENT TO PRECIPITATE ASPHALTENES

The amount of pentane designated to precipitate the asphaltenes was initially 100 ml to dissolve the asphalt sample, and a total of approximately 250 to 300 ml after all washings. It was observed that after 300 ml of pentane, the filtrate was still coming through the funnel very dark in color, which indicated that the maltene fraction was still being held onto the asphaltene fraction. The asphaltenes are highly polar molecules and are capable of hydrogen bonding to the polar molecules of the maltene fraction. Therefore, in order to separate total maltenes, the amount of pentane was increased. It was found that using a total of 1500 ml of pentane was sufficient to recover the maltene fraction for a variety of asphalts with varying amounts of polars and asphaltenes. If the filtrate is clear before 1500 ml is used, it can be assumed that the maltenes are completely separated from the asphaltenes and pentane addition can be discontinued at that time. The amount of pentane used is dependent upon the percentage of asphaltenes in the sample, that is, the more asphaltenes, the more pentane required.

SAMPLE SIZE

Sample size is an important factor when the samples contain high polar percentages. As stated in the ASTM procedure, when the polar content exceeds 20 percent, a reduction in sample size is warranted since the capacity of the clay column for adsorbing polars is limited. A 5-gram sample is the upper limit for highly polar samples, but a 2.5-gram sample insures that the clay column will not be overloaded. A 2.5-gram sample has produced excellent repeatability for all materials tested.

SOLVENT SYSTEM FOR POLARS

The original ASTM method calls for a maximum of 300 ml of a 50/50 mixture of benzene to acetone by volume to strip the polar column. Benzene was replaced by toluene because of the carcinogenic classification of benzene. The eluent from the clay column was still dark in color after addition of 300 ml of solvent, so the percentages were altered to 30 percent toluene and 70 percent acetone, as well as the amount of solvent used was increased to 1500 ml, or until the eluent was clear. The use of acetone has caused some concern by several researchers consulted. The acetone adds ketone functionality to the fraction which manifests itself as additional carbonyl absorbances when using infrared spectroscopy as an additional technique. Methanol was tried as a replacement for acetone, however, toluene/acetone has a solubility parameter closer to benzene/acetone and was considered to give better separation.

SOLVENT SYSTEMS FOR AROMATICS

It was necessary to develop a solvent system to strip the aromatic column and achieve mass balance. A 30/70 percent by volume methanol/toluene mixture was used. Care is required to ensure that the methanol is dry and that no more than 30 percent of methanol is used; since the silica gel reacts with the water and/or methanol and results in heating of the column. This can result in fracture of the column at the fritted joint if the column is not properly constructed.

ADDITIONAL FINAL ELUENT

A final modification to these two solvent systems for the polars and aromatics is as follows: An additional 100 ml of pure toluene is charged to the aromatic column, and 200 ml of methylene chloride is charged to the polar column as the final eluents. These additions will insure that all material is being efficiently stripped from the column.

ELIMINATION OF CALCIUM CHLORIDE

The last modification to the Clay-Gel technique involves the use of calcium chloride and a separatory funnel to remove water from the polar compound eluent. This step was discarded because it was cumbersome and time consuming. By drying the solvents with molecular sieves before using, the need to perform this step was eliminated.

ROTARY EVAPORATOR

The use of a rotary evaporator for solvent evaporation has lessened the time factor significantly and made solvent removal more efficient and complete.

END

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